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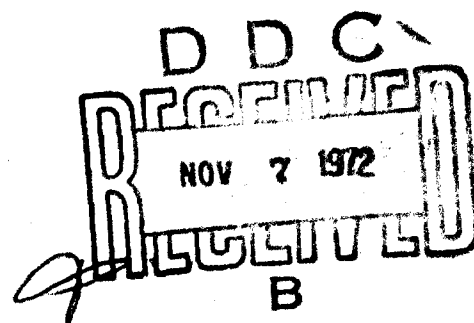
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MANUFACTURING METHODS FOR
CARBOXY NITROSO RUBBER

C. D. Padgett
J. R. Patton

PCR, INC.
Gainesville, Florida 32601



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FOREWORD

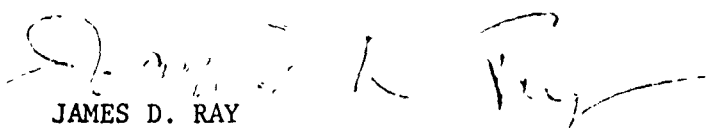
The work described in this report was performed under Contract No. F33615-71-C-1166. This contract was initiated under Project No. 342-9, "Manufacturing Methods for Carboxy Nitroso Rubber," and administered by the Non-Metals/Composites Branch, Manufacturing Technology Division of the Air Force Materials Laboratory, with Mr. D. F. Starks acting as project engineer.

The work described in this report was carried out by Mr. C. D. Padgett, Project Director, and Mr. J. R. Patton, Research Chemist, with the technical assistance of Messrs. R. W. Tillman, M. Brown, and L. Stocker. Engineering assistance was supplied by Mr. D. A. Adams, Mr. W. E. Reneke, and Mr. R. A. Keppel.

Appreciation is expressed to Messrs. J. K. Sieron and T. Wical of the Elastomers Branch, AFML, for the compounding and mechanical properties determinations.

This is a Final Report covering work conducted from January 1, 1971 through May 31, 1972.

This technical report has been reviewed and is approved.



JAMES D. RAY
Chief, Non-Metals/Composites Branch
Manufacturing Technology Division
Air Force Materials Laboratory

ABSTRACT

This concludes the program establishing manufacturing methods for Carboxy Nitroso Rubber by "thin film bulk polymerization." The objectives were to evaluate at the pilot plant level the materials, chemical, engineering, and processing requirements for a production capability of thirty pounds of CNR per week and applicable for scale-up to 50,000 to 100,000 pounds per year. This was a five phase program during which the following functions were performed: Phase I, Production of Perfluoroglutaric Acid (PFGA); Phase II, Production of Nitrosoperfluorobutyric Acid (NPBA); Phase III, Production of Trifluoronitrosomethane (CF_3NO); Phase IV, Thin Film Polymerization of Carboxy Nitroso Rubber (CNR); and Phase V, Evaluation and Projected Scale-up Pilot Plant. Demonstrations by the selected process were conducted that illustrated the reproducibility of yields and quality of product and for the production of approximately ninety pounds of the CNR product.

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I. INTRODUCTION

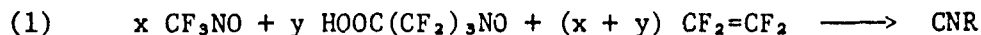
This document is the final technical report for the period January 1, 1971 through May 31, 1972 on the program entitled "Manufacturing Methods for Carboxy Nitroso Rubber," Contract No. F33615-71-C-1166. The objective of this program was to put into operation and evaluate a pilot plant capable of producing 30 lbs/wk of carboxy nitroso rubber utilizing the technique of neat (bulk) polymerization. It was the purpose of the pilot plant to establish an economical manufacturing process for the production of 100,000 lbs/year of carboxy nitroso rubber.

The program was divided into five phases, some of which were carried out concurrently with others. These phases are: Phase I, Production of Perfluoroglutaric Acid (PFGA); Phase II, Production of Nitrosoperfluorobutyric Acid (NPBA); Phase III, Production of Trifluoronitrosomethane (CF_3NO); Phase IV, Thin-Film Polymerization of Carboxy Nitroso Rubber (CNR); and Phase V, Evaluation and Projected Scale-up of Pilot Plant.

II. DISCUSSION

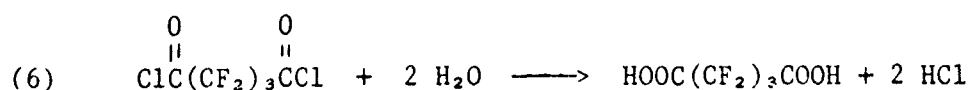
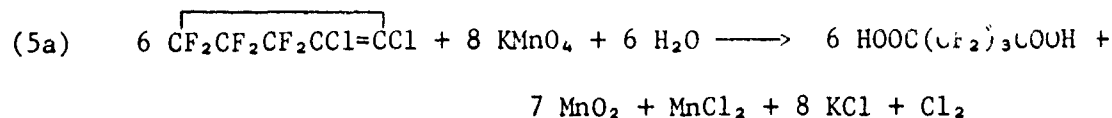
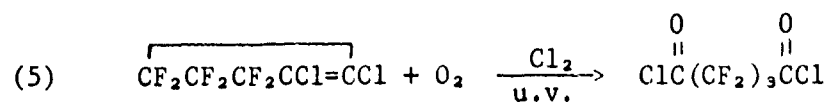
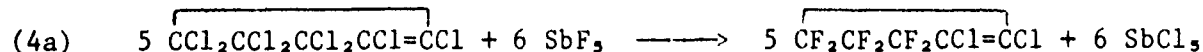
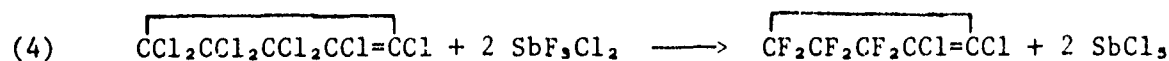
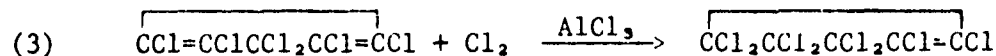
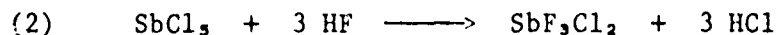
A. Reaction Systems

The neat polymerization of carboxy nitroso rubber monomers may be shown as follows:

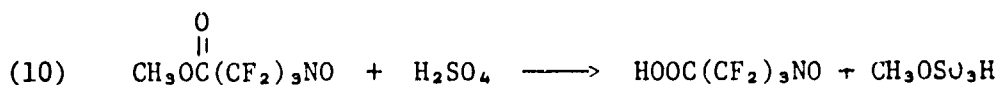
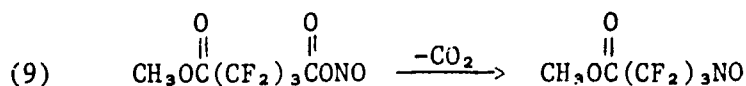
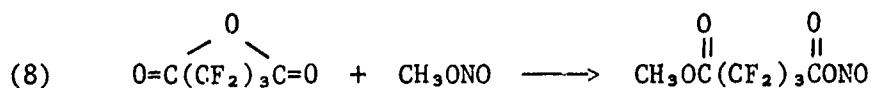
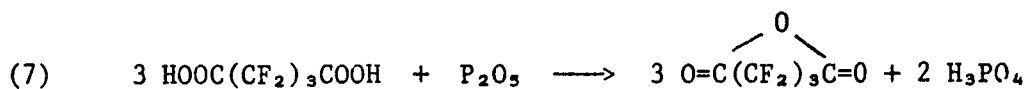


Tetrafluoroethylene is commercially available, but the other two monomers must be synthesized. Therefore, in addition to the polymerization reaction, it was necessary to establish an economical synthesis for CF_3NO and $\text{HOOC}(\text{CF}_2)_3\text{NO}$. The following systems were chosen for evaluation.

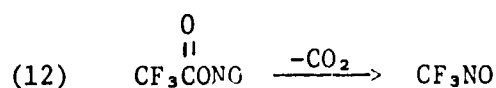
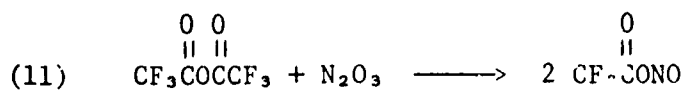
Synthesis of PFGA



Synthesis of NPBA

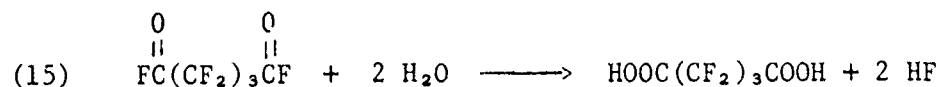
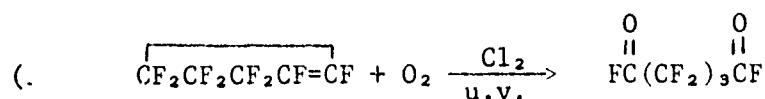
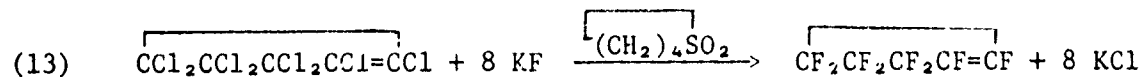


Synthesis of CF₃NO

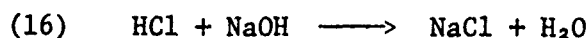


An alternate route for the synthesis of PFGA using KF as the fluorinating agent was also evaluated.

Alternate Synthesis of PFGA



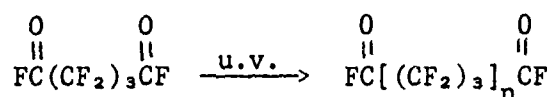
In addition to the above, several other reactions were required for the neutralization of HCl and HF, removal of CO₂, and synthesis of CH₃ONO.



B. Phase I, Production of Perfluoroglutaric Acid (PFGA)

Several chlorinations of $\text{CCl}=\text{CClCCl}_2\text{CCl}=\text{CCl}$ have been carried out on a 20-30 kg scale to give 99-100% yields of $\text{CCl}_2\text{CCl}_2\text{CCl}_2\text{CCl}=\text{CCl}$. The reaction (3) goes readily at atmospheric pressure by bubbling Cl₂ into a flask of heated perchlorocyclopentadiene containing a small amount of aluminum chloride. The perchlorocyclopentene was converted to PFGA by two general routes. The first makes use of several of the reactions (2) - (6), and the alternate route utilizes reactions (13)-(15). Reactions (13)-(15) were evaluated first while the equipment for reactions (2) - (6) was being fabricated and installed.

It was found that reaction (13) would give an 80% yield of $\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}=\text{CF}$ using a $\text{CCl}_2\text{CCl}_2\text{CCl}_2\text{CCl}=\text{CCl}/\text{KF}$ mole ratio of 1/1.1 and a KF/sulfolane ratio of 1 g/1 ml. An 80% recovery of sulfolane was achieved. Reaction (14) was very rapid but an extremely low yield of the acid fluoride was obtained. This was thought to be due to the oligomerization of the acid fluoride in u.v. light¹:



When reaction (14) was combined with (15) and (17) by carrying out the oxidation in the presence of a solution of CaCl_2 , a 53% yield of PFGA was obtained. Since previous experience has shown that the hydrolysis of $\text{ClC}(\overset{\text{O}}{\parallel})_2\text{CCl}$ is a high yield reaction, it is arbitrarily assumed that reaction (14) gave a 53% yield and that reaction (15) and (17) gave 100% yields. Reaction (14) was carried out in standard laboratory glassware which showed no weight loss as a result of the reaction. Samples of 316 stainless steel and carbon steel were included in one reaction mixture with the following results:

<u>Material</u>	<u>Initial Wt,</u> <u>g</u>	<u>Final Wt,</u> <u>g</u>	<u>Wt. Loss</u> <u>g</u>	<u>% Loss</u>
316 stainless steel	1.1400	1.1395	0.0005	0.044
carbon steel	1.0547	1.0508	0.0039	0.37

Based on the above results, a preliminary comparison between the estimated materials cost and labor cost of the KF fluorination route and the SbCl_5/HF fluorination route was made. These values are shown in Tables I and II. It may be seen that the materials cost for the KF fluorination route is almost twice the materials cost for the SbCl_5/HF route and that the labor cost is 1.5 times greater. It should be noted that this is not a strictly accurate comparison since the SbCl_5/HF fluorination route was later abandoned in favor of fluorination with SbF_5 . However, even though the use of SbF_5 increases the material cost, it reduces the labor cost.

The apparatus shown in Figure 1 was designed to carry out reactions (2) - (4) for the production of $\text{CF}_2\text{CF}_2\text{CF}_2\text{CCl}=\text{CCl}$. The general reaction procedure is described as follows.

The reaction kettle (25 gal capacity) is charged with SbCl_5 and then heated by oil circulating through the kettle jacket. Anhydrous HF is then charged from the cylinder shown in the upper left corner of Figure 1. The reflux condenser fitted to the kettle lid is cooled by circulating brine. The HCl generated in reaction (2) escapes through the

TABLE I

MATERIAL COST FOR PRODUCTION OF 5.89 LB OF PFGA

Material Cost for Production of 5.89 lb of PFGA Using SbCl_5 /HF Fluorination Route

<u>Material</u>	<u>Weight (lb)</u>	<u>Unit Cost</u>	<u>Total Cost</u>
SbCl_5	3.82*	\$0.57/lb	\$2.18
HF	7.57	0.36/lb	2.73
C_5Cl_6	15.83	0.30/lb	4.75
Cl_2	4.12	0.14/lb	0.58
O_2	1.10	0.13/lb	0.14
NaOH	17.38	0.07/lb	<u>1.27</u>
			\$11.65

*Weight of SbCl_5 lost assuming a 90% recovery.

Material Cost for Production of 5.89 lb of PFGA Using KF Fluorination Route

<u>Material</u>	<u>Weight (lb)</u>	<u>Unit Cost</u>	<u>Total Cost</u>
C_5Cl_6	15.97	0.30/lb	4.79
Cl_2	4.15	0.14/lb	0.58
KF	26.87	0.40/lb	10.75
$(\text{CH}_2)_4\text{SO}_2$	(0.64 gal)*	10.00/gal	6.40
O_2	1.48	0.13/lb	0.19
CaCl_2	2.72	0.07/lb	<u>0.19</u>
			\$22.90

*Amount of sulfolane lost assuming an 80% recovery.

TABLE II

ESTIMATED MAN-HOURS REQUIRED FOR PRODUCTION OF 5.89 LB OF PFGA

Estimated Man-Hours Required for Production of 5.89 lb of PFGA Using
SbCl₅/HF Fluorination Route

<u>Operation</u>	<u>Time (Man-Hours)</u>
Reaction (2)	2
Reaction (3)	4
Reaction (4)	2
Combination Reactions (5) and (6)	4
Isolate PFGA	<u>4</u>
Total	16

Estimated Man-Hours Required for Production of 5.89 lb of PFGA Using KF
Fluorination Route

<u>Operation</u>	<u>Time (Man-Hours)</u>
Reaction (3)	4
Reaction (13)	8
Recover sulfolane	2
Clean and Set-up Equipment for Rerun	2
Combination Reactions (14) and (15)	4
Isolate PFGA	<u>4</u>
Total	24

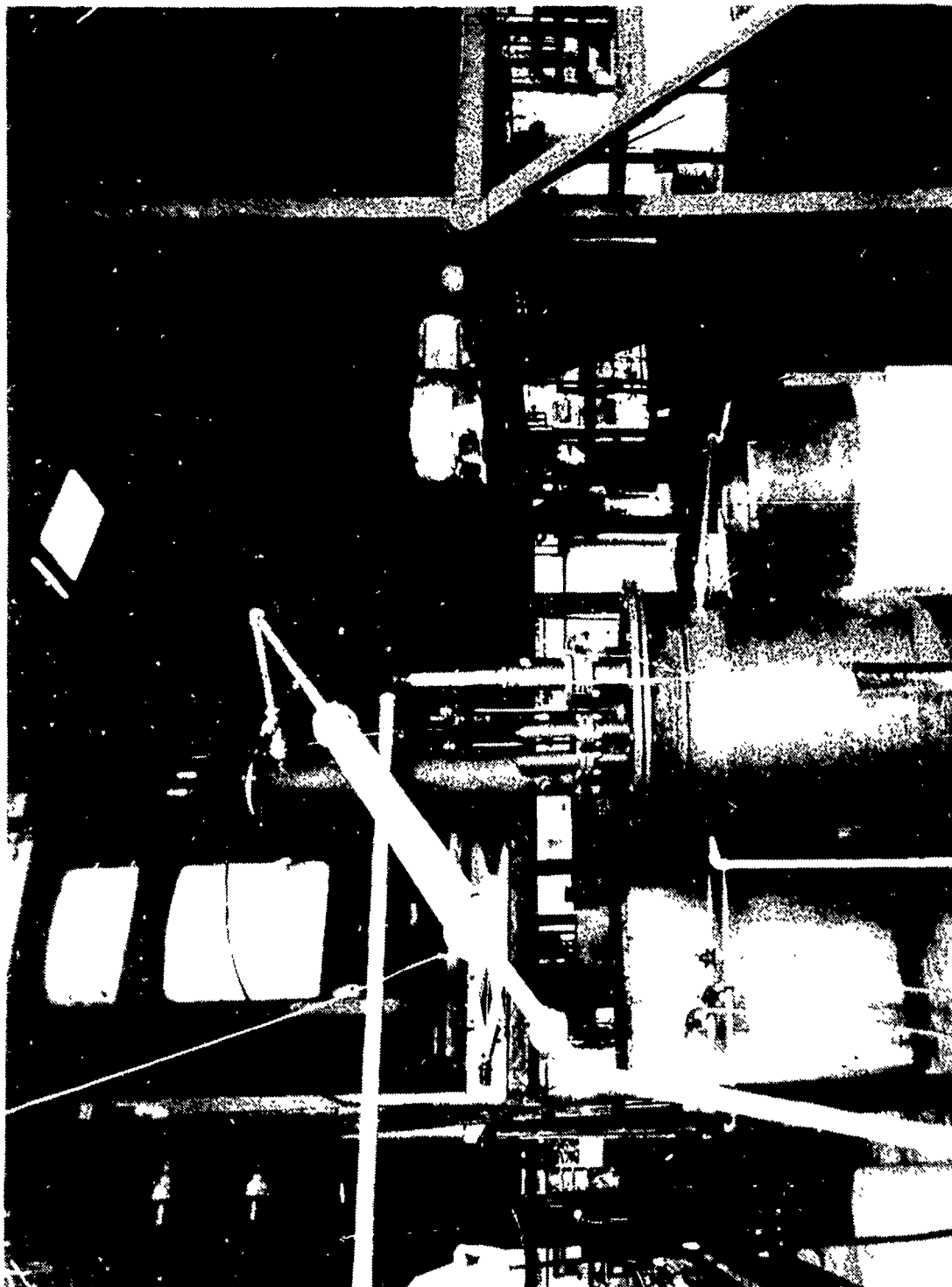


Figure 1 - Reaction Kettle for Fluorination with Antimony Salts

top of the condenser to a solution of NaOH. After reaction is completed the reflux condenser is allowed to warm, and excess HF is also neutralized in the NaOH solution. The $\text{CCl}_2\text{CCl}_2\text{CCl}_2\text{CCl}=\text{CCl}$ is then added through one of the flanged adapters on the kettle top, and the solution is again heated to effect reaction (4). After the fluorination is completed a take-off condenser is attached at the bottom of the reflux condenser, and the $\text{CF}_2\text{CF}_2\text{CF}_2\text{CCl}=\text{CCl}$ is stripped from the reaction mixture.

In the first trial run the kettle was charged with antimony pentachloride which was then stirred as anhydrous HF was dripped into the mixture to effect reaction (2). After the HF addition was complete, the kettle was heated to 80° overnight. This was followed by the rapid addition of perchlorocyclopentene and again heating at 80° overnight to effect reaction (4). The temperature for the reaction vessel was then raised to 180° and the product was stripped off. The product was a mixture of solid and liquid which was shown by infrared spectrum to contain neither the desired $\text{CF}_2\text{CF}_2\text{CF}_2\text{CCl}=\text{CCl}$ nor the starting material, $\text{CCl}_2\text{CCl}_2\text{CCl}_2\text{CCl}=\text{CCl}$, but rather a mixture of partially fluorinated cyclopentenes. While the solid product was not fully identified, it was established that it was not the perchlorocyclopentene but an antimony compound. It was thought that a better reaction might be effected if the C_5Cl_8 was mixed with the SbCl_5 before this latter compound was reacted with HF. This was the procedure followed in the second reaction.

The kettle was again charged with SbCl_5 , and then the $\text{CCl}_2\text{CCl}_2\text{CCl}_2\text{CCl}=\text{CCl}$ was added. The HF was dripped into the reaction mixture and it remained near ambient temperature. After the HF addition was completed, the mixture was heated at 85° for 18 hrs. It was then strip distilled to again give a mixture of solid and liquid. Workup of this material gave a 25% conversion to $\text{CF}_2\text{CF}_2\text{CF}_2\text{CCl}=\text{CCl}$.

The reaction was repeated on a larger scale with the additional modification that this time the HF addition tube opened beneath the surface of the liquid reactants. It was thought that perhaps the HF was simply volatilizing from the reaction kettle before fluorination could occur. In this latter reaction the exit gases were analyzed for % HCl vs % HF as a further indication of degree of fluorination. This analysis showed that during the main course of the reaction the gases were 80-95%

HCl and only 5-20% HF. However, workup of the product gave a mixture of solid and liquid which again gave a low (20%) yield of $\text{CF}_2\text{CF}_2\text{CF}_2\text{CCl}=\text{CCl}$.

Fresh SbCl_5 was purchased and upon analysis was found to contain less than 0.1% Sb^{3+} . The kettle was charged with 109 lb of SbCl_5 and 52 lb of C_5Cl_8 , but a break in a line connected to a dip tube resulted in some loss of material. The remaining contents were found to weigh 99.5 lb and were assumed to be a homogeneous mixture of 67.4 lb of SbCl_5 and 32.1 lb of C_5Cl_8 . The reaction was continued with this mixture in a manner similar to earlier fluorinations (details given in Experimental section of this report) to give a 32% yield of $\text{CF}_2\text{CF}_2\text{CF}_2\text{CCl}=\text{CCl}$. Analysis of the kettle residue showed 13.6% Sb^{3+} . This mixture was chlorinated until the amount of Sb^{3+} was lowered to 1.4%.

After the kettle residue was lowered to 1.4% Sb^{3+} , it was charged with an additional 51 lb of C_5Cl_8 , and a second fluorination was carried out as before. This time only a 16% yield of $\text{CF}_2\text{CF}_2\text{CF}_2\text{CCl}=\text{CCl}$ was obtained.

The kettle was thoroughly cleaned and again charged with SbCl_5 . The fluorination was carried out as before, and after 11 days a 41% yield of $\text{CF}_2\text{CF}_2\text{CF}_2\text{CCl}=\text{CCl}$ was obtained.

It is known that the reaction of SbCl_5 with HF will not give SbF_5 in the presence of iron.² However, a mixed chloride-fluoride salt of antimony is obtained which shows a fluorine analysis indicative of SbF_3Cl_2 . It is assumed that this compound will effect reaction (4).

Two major difficulties were encountered with reactions (3) and (4). The first was the apparent slowness of reaction (2). For example, in the fluorination mentioned above, the reaction times varied from two to eleven days. If the rate of HF addition to the kettle was speeded up, it simply resulted in a cooling of the kettle contents due to refluxing HF. The second difficulty was the low yields of $\text{CF}_2\text{CF}_2\text{CF}_2\text{CCl}=\text{CCl}$. This posed the question of how readily $\text{CCl}_2\text{CCl}_2\text{CCl}_2\text{CCl}=\text{CCl}$ or $\text{CCl}=\text{CClCCl}_2\text{CCl}=\text{CCl}$ may be fluorinated if it is known that an antimony fluoride is present and whether or not the presence of iron might interfere with the fluorination.

In order to answer these questions a 5500-ml kettle similar to the 25-gal kettle was constructed. This kettle was charged with 3250 g of SbF_3 and 1290 g of C_3Cl_8 and heated at 90° for 16 hrs. The temperature was then raised to 95° and 755 g (82% yield) of $\text{CF}_2\text{CF}_2\text{CF}_2\text{CCl}=\text{CCl}$ was obtained. The kettle was then cooled to 90° and 694 g of $\text{CCl}=\text{CClCCl}_2\text{CCl}=\text{CCl}$ was added and heated at this temperature for 16 hours. The kettle temperature was then raised to 110° and 396 g of 88% $\text{CF}_2\text{CF}_2\text{CF}_2\text{CCl}=\text{CCl}$, representing a 58% yield, was obtained.

Aside from the fact that either the pentene or pentadiene may be easily fluorinated with SbF_3 , it was also noted that in this reaction the kettle contents were only heated to $\sim 100^\circ$ to drive off the $\text{C}_3\text{Cl}_2\text{F}_6$; in reactions where SbCl_3 was utilized, the kettle contents had to be heated to $\sim 170^\circ$ in order to drive off $\text{C}_3\text{Cl}_2\text{F}_6$.

Two additional reactions of SbF_3 with C_3Cl_8 in the 5500-ml kettle gave $\text{CF}_2\text{CF}_2\text{CF}_2\text{CCl}=\text{CCl}$ yields in the 80% range. However, several attempts to utilize this smaller kettle for the $\text{SbCl}_3/\text{HF}/\text{C}_3\text{Cl}_8$ system again gave low yields of $\text{CF}_2\text{CF}_2\text{CF}_2\text{CCl}=\text{CCl}$.

On the basis of the above results it was concluded that for the purposes of the cost evaluation in Phase V, reaction (4a) should be used. In Table VII it is seen that the cost of SbF_3 represents \$2.18 of the cost of each pound of CNR. It is estimated that this figure could be reduced as much as \$0.50 - \$0.75 per pound if reactions (2) and (4) could replace (4a).

Two oxidations of $\text{CF}_2\text{CF}_2\text{CF}_2\text{CCl}=\text{CCl}$ with KMnO_4 were carried out. In the first reaction 100 g of $\text{C}_3\text{Cl}_2\text{F}_6$ was oxidized by adding small increments of KMnO_4 to a refluxing mixture of $\text{C}_3\text{Cl}_2\text{F}_6$ and H_2O . After the purple color of permanganate had disappeared the mixture was filtered to remove MnO_2 and give an aqueous solution of $\text{HOOC}(\text{CF}_2)_3\text{COOH}$ or $\text{KOO}(\text{CF}_2)_3\text{COOK}$. An attempt to isolate the acid was unsuccessful. The solution was made strongly acidic with H_2SO_4 and then extracted with ethyl ether. However, the ether extracted some of the H_2SO_4 and not all of the $\text{HOOC}(\text{CF}_2)_3\text{COOH}$. It appears that $\text{HOOC}(\text{CF}_2)_3\text{COOH}$ is more soluble in H_2O than in any solvent immiscible with H_2O , thereby making extraction extremely difficult.

Since this project is not concerned with producing $\text{HOOC}(\text{CF}_2)_3\text{COOH}$ but with reaction products of this compound, another KMnO_4 oxidation was carried out with the goal of isolating $\text{O}=\text{C}(\text{CF}_2)_3\text{C}=\text{O}$ rather than the acid. The oxidation was run as before and again the product mixture was filtered to give an aqueous solution of $\text{HOOC}(\text{CF}_2)_3\text{COOH}$ or the potassium salt. The solution was then acidified with HCl and evaporated to dryness to give a mixture of KCl and $\text{HOOC}(\text{CF}_2)_3\text{COOH}$. This mixture was dehydrated by heating with P_2O_5 ; a 60% yield of $\text{O}=\text{C}(\text{CF}_2)_3\text{C}=\text{O}$ was obtained.

Since the oxidation of $\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}=\text{CF}$ with $\text{O}_2/\text{Cl}_2/\text{u.v.}$ was successfully carried out in the presence of water to give $\text{HOOC}(\text{CF}_2)_3\text{COOH}$, this was the first approach taken with the photolytic oxidation of $\text{CF}_2\text{CF}_2\text{CF}_2\text{CCl}=\text{CCl}$. The $\text{C}_5\text{F}_6\text{Cl}_2$ was dripped into a flask containing hot water and fitted with a Vycor immersion well housing a 400 watt u.v. lamp. The water was heated above 90° so that the pentene would vaporize. A mixture of O_2/Cl_2 was continuously admitted to the system. However, after 3.8 moles of $\text{C}_5\text{F}_6\text{Cl}_2$ had been photolyzed in the presence of 9 moles of O_2 and 1 mole of Cl_2 , there was no evidence for the formation of the acid. The reaction was attempted again by having all of the $\text{C}_5\text{F}_6\text{Cl}_2$ and a small amount of H_2O in a Vycor flask irradiated with an internal u.v. source and bubbling in the O_2/Cl_2 mixture. In this setup all of the $\text{C}_5\text{F}_6\text{Cl}_2$ was swept from the system and there was again no evidence for the formation of the acid.

After these unsuccessful oxidation attempts, several reactions were carried out on a small scale using 1-liter Vycor flasks. The flasks were charged with $\text{C}_5\text{F}_6\text{Cl}_2$ and a stirring bar, cooled in liquid air and evacuated. This was followed by warming to ambient temperature, charging with O_2 and Cl_2 and then stirring the mixture in the presence of sunlight. In these small scale runs a 100% conversion to $\text{Cl}\overset{\text{O}}{\underset{\text{O}}{\text{C}}}(\text{CF}_2)_3\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{Cl}$ was obtained. It was also found that the oxidation would proceed as well in Pyrex as in Vycor.

The reaction was scaled up to a 12-liter flask, and several runs were made utilizing both sunlight and u.v. lamps. Conversions ranged from 50 to 90%, depending upon the length of irradiation, with recovered $\text{C}_5\text{F}_6\text{Cl}_2$ normally accounting for a 100% yield. One of these oxidations exhibited singular behavior in that all of the pentene was consumed but only a 66% yield of

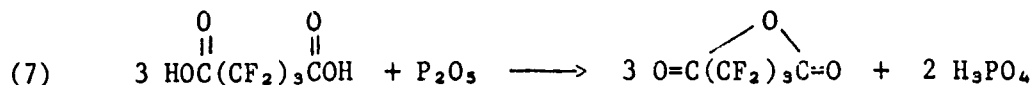
$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{ClC}(\text{CF}_2)_3\text{CCl} \end{array}$
 was obtained. Distillation of the product mixture gave a higher boiling fraction which appeared to be a mixture of acid chlorides formed by the oligomerization of $\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{ClC}(\text{CF}_2)_3\text{CCl} \end{array}$.

Although the photolytic oxidation of $\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}=\text{CF}$ was found to be almost instantaneous, the oxidation of $\text{CF}_2\text{CF}_2\text{CF}_2\text{CCl}=\text{CCl}$ required a period of several days for reasonable conversion to the acid chloride. An attempt was made to speed up the process by increasing the contact between the reacting pentene and oxygen. This was done by fitting the reaction flask with a 4-ft column and pumping the pentene from the bottom of the flask to the top of the column. Then a mixture of O_2 and Cl_2 was passed up through the column as the liquid flowed down the walls. Two reactions were run in this manner and in both of them the tubing used to pump the pentene to the top of the column broke before the reaction was completed. Analysis of recovered material showed a 60% conversion to $\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{ClC}(\text{CF}_2)_3\text{CCl} \end{array}$ after five hours in the first run, but only a 20% conversion was obtained after ten hours in the second reaction. Although subsequent runs utilized a static system rather than the flow system, indications are that the oxidation time can be reduced by this method. The simplicity of the photolytic oxidation of $\text{CF}_2\text{CF}_2\text{CF}_2\text{CCl}=\text{CCl}$ plus the high (95%) yield of product renders the KMnO_4 oxidation of this material economically unfeasible.

The conversion of $\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{ClC}(\text{CF}_2)_3\text{CCl} \end{array}$ to $\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{HOC}(\text{CF}_2)_3\text{COH} \end{array}$ (6) is simply a matter of dropping the acid chloride into warm water. After the addition is completed HCl and excess H_2O is removed under vacuum to leave a 100% yield of the perfluoroglutaric acid.

C. Phase II, Production of Nitrosoperfluorobutyric Acid (NPBA)

Perfluoroglutaric anhydride was consistently obtained in good (95%) yield by adding small increments of P_2O_5 to a flask in which the heated acid was stirred.

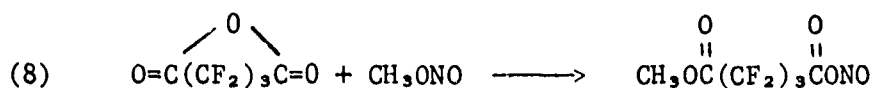


The anhydride is stripped from the reaction mixture as the P_2O_5 is added. It was found that one gram of P_2O_5 was sufficient to dehydrate one gram of the acid.

Methyl nitrite was consistently prepared in good (85%) yield by adding H_2SO_4 to a water solution of CH_3OH and $NaNO_2$:

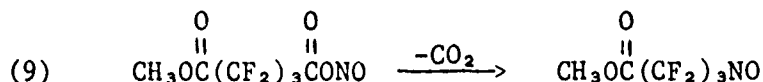


The addition of methyl nitrite to perfluoroglutaric anhydride is a smooth reaction which produces carbomethoxyperfluorobutyryl nitrite (CMPBN)



in nearly 100% yield. The methyl nitrite is simply bubbled into the heated (65°) anhydride, and then the mixture is stirred overnight. The methyl nitrite is used in slight excess to insure complete reaction of the anhydride, and the excess is removed under vacuum. Analysis of the CMPBN by NMR indicated a purity of >99%.

Methyl nitrosoperfluorobutyrate, MNPB, is prepared by the decarboxylation of CMPBN.



In earlier work the nitrite ester had been decarboxylated by both pyrolysis³ and photolysis⁴. Using either method a vacuum must be maintained in order to remove the product from the reaction zone. Also, both methods produce by-products which will interfere with the reaction if they are not removed as formed. The apparatus shown schematically in Figure 2 was designed to keep the build up of these by-products at a minimum by continuously removing them through the bottom of the reactor. A film of the nitrite ester is allowed to flow down a water-cooled Pyrex tube housing a u.v. lamp. A vacuum is maintained so that the nitroso ester is removed as it is formed. The drain at the bottom allows for removal of the high boiling by-products. However, during several trial runs two major difficulties were encountered: the reaction was extremely slow, and yields of the nitroso ester were in the 20% range.

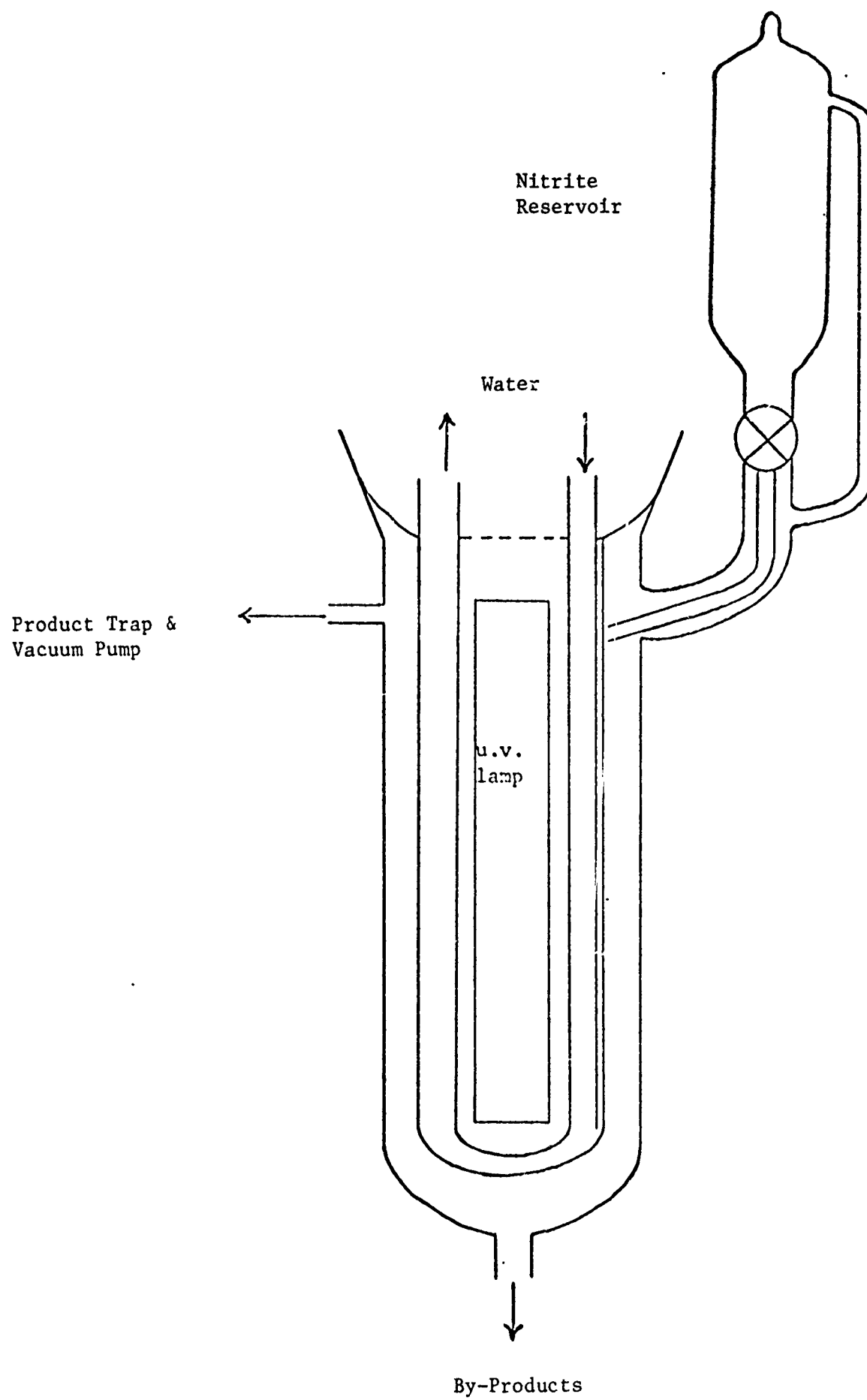


Figure 2. Photolysis Apparatus

Past PCR work concerned with the pyrolysis of $\text{CH}_3\text{O}_2\text{C}(\text{CF}_2)_3\text{CO}_2\text{NO}$ has involved passing the material through an externally heated column while maintaining a vacuum. The major difficulty with this type of apparatus is that a slight change in any part of the setup (such as change in pressure, length or diameter of column, temperature, or any changes necessary for scale-up) causes a drastic change in product yield. This same difficulty was experienced in early CF_3NO production efforts where the problem was partially solved by the use of a refluxing liquid as the heat source for decarboxylation. In the first trial run utilizing a similar set-up, CMPBN was decarboxylated to give a 47% yield of MNPB.

In the decarboxylation of $\text{CF}_3\overset{\text{O}}{\parallel}\text{CONO}$, FC-43 (perfluorotributyl amine) is used as the refluxing liquid. However, this decarboxylation is conducted at atmospheric pressure whereas the decarboxylation of CMPBN is carried out at ~ 10 mm pressure. Consequently, a much higher boiling inert liquid is required for this latter decarboxylation. A suitable material was found to be Fomblin (Montecatini-Edison trademark for its perfluorinated polyether fluids) fractionated to give a bp = $180\text{--}210^\circ/10$ mm. The CMPBN decarboxylation is then run at ~ 10 mm pressure.

As noted above, the pyrolysis of CMPBN produces a by-product (essentially the tri-ester $[\text{CH}_3\overset{\text{O}}{\parallel}\text{C}(\text{CF}_2)_3]_2\text{NO}(\text{CF}_2)_3\overset{\text{O}}{\parallel}\text{COCH}_3$) which must be removed from the reaction zone. After several trial runs and modifications, the apparatus shown schematically in Figure 3 was used to produce MNPB in yields varying from 36 to 54% but normally in the 45% range. Since the Fomblin is more dense than the tri-ester this latter material could not be removed by use of a distillation head alone without removing excessive amounts of Fomblin. However, when the setup was modified as shown in Figure 3 the Fomblin could be returned to the decarboxylation chamber as the tri-ester was removed.

It was found that ~ 250 g of CMPBN could be decarboxylated in an 8-hr period using a 500-ml flask fitted with a 15 mm x 18" column and containing 250 g of Fomblin.

The apparatus was weighed and visibly inspected before and after several decarboxylations. There was no appreciable weight loss or etching of the glass. Weight loss of Fomblin was also negligible.

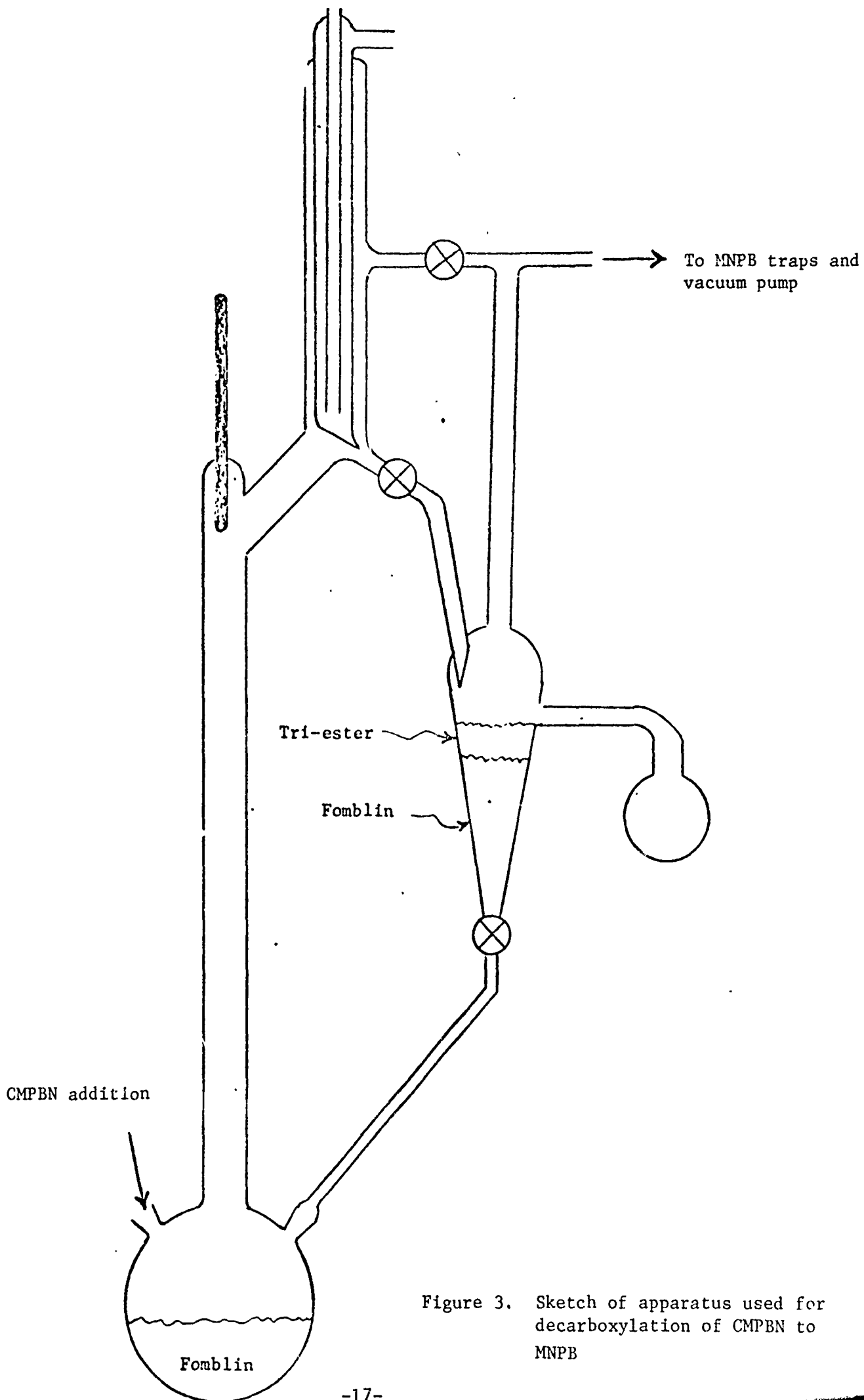
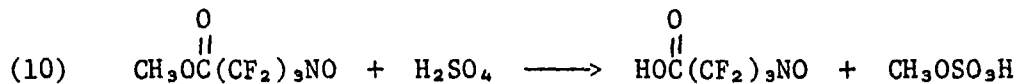


Figure 3. Sketch of apparatus used for decarboxylation of CMPBN to MNPB

Utilizing a slight variation in the method established by earlier workers,⁴ MNPB was hydrolyzed to NPBA in 90% yields.

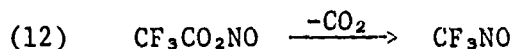
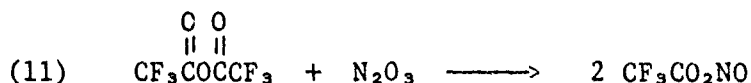


The ester can also be hydrolyzed in water, but isolation difficulties are experienced. The best hydrolysis results were obtained by stirring MNPB with 15 times its weight of 98-99% H₂SO₄ heated at 85°C for six hours and then removing the product under full vacuum to traps cooled to -78°. The product is then distilled under vacuum on an Oldershaw column to give a material containing ~97% NPBA and ~3% MNPB. The acid is storable in glass at room temperature and does not readily decompose on exposure to air or light.

D. Phase III, Production of Trifluoronitrosomethane (CF₃NO)

Information generated in earlier Government-sponsored programs^{3,4,5,6,7} is summarized below.

The most practical route for the production of trifluoronitrosomethane is via the reaction of trifluoroacetic anhydride with nitrogen trioxide to produce trifluoroacetyl nitrite and the subsequent pyrolysis of this material to trifluoronitrosomethane.



Reaction (11) proceeds smoothly by adding either reactant to the other at temperatures ranging from -78 to +25°C. Since both the anhydride and nitrogen trioxide are volatile (b.p. = 40° and 3.4°, respectively) a reaction temperature of about -10° is preferred. The N₂O₃ must be kept in the liquid phase as it dissociates to NO and NO₂ in the gas phase.

The reaction proceeds equally well using either reactant in excess or using stoichiometric amounts of both. The pure nitrite is amber colored, and this same color will be observed if the anhydride is used in excess. If the N_2O_3 is used in excess, it can be observed that the reaction is complete when the blue color of this material persists. The nitrite is usually prepared by adding either reactant (in the liquid phase) to the other while the reaction mixture is cooled in the range -78° to -10° . It is then adjusted to a temperature of -20° and a vacuum (~ 1 mm Hg) applied to remove unreacted material. Yields of the pure nitrite are nearly quantitative.

The nitrite has been stored for as long as one month at $-10^\circ C$ with no adverse effect upon yield or purity of the CF_3NO obtained in the subsequent decarboxylation. The material has also been stored for two weeks at $0^\circ C$ with no adverse results. However, storage for two weeks at $40^\circ C$ resulted in a 45% reduction in percent yield of CF_3NO . All storage was in glass vessels shielded from light and in the absence of atmospheric oxygen or moisture.

It has been determined that CF_3COONO will detonate with about the same explosive power as nitromethane or TNT or about 0.1 to 0.2 of the explosive power of nitroglycerine. Tests have indicated that the nitrite will ignite on initiation at about 65° in concentrations greater than 50% with N_2 as a diluent. Attempts to ignite the vapors of CF_3CO_2NO under conditions similar to those employed during the production of CF_3NO , that is dilution with vapors of refluxing perfluorotributyl amine, gave no ignition with a Tesla coil induced spark. Studies of detonation wave propagation showed that stainless steel up to 11/16 in. ID would not propagate the wave. It is to be expected that larger diameters of plastic or glass tubing could be used.

In studying the pyrolysis of CF_3CO_2NO , the preferred temperature range was found to be $150-210^\circ$. Refluxing perfluorotributyl amine (FC-43) was found to be an excellent decarboxylating medium for several reasons: it has a boiling point of 184° ; even though it is an expensive material, very little FC-43 is lost during decarboxylation; and finally, dilution of CF_3CO_2NO vapors with those of FC-43 reduces the hazard of ignition or detonation. The few explosions which have been reported in decarboxylation facilities

utilizing FC-43 have been attributed to a heat feedback to the nitrite reservoir. Several other liquids have been tried in the place of FC-43, including both hydrocarbons and halocarbons, but none of them has proven to be as satisfactory.

The first decarboxylations were carried out in the laboratory using borosilicate glass. Various metals were tested in an attempt to find a more suitable material for construction of large scale reactors. It was found that copper, steel, nickel, and monel are badly corroded at the pyrolysis temperatures. Stainless steel (316) is compatible with the nitrite at room temperature, but it also corrodes at the elevated temperature required for decarboxylation. Thus, borosilicate glass appears to be the best material of construction for the decarboxylation reactor, and glass, polyethylene, Teflon, or 316 stainless steel may be used for transfer lines at room temperature.

The average conversion of $\text{CF}_3\text{CO}_2\text{NO}$ to CF_3NO is 50%. As many as eighteen other compounds have been found as impurities in the product mixture. The major impurities are CO_2 and NO_2 ; others found are CF_3NO_2 , $(\text{CF}_3\text{NO})_2$, nitrogen oxides, fluorocarbons up to C_4F_{10} , COF_2 , CF_3OCF_3 , etc. It has been found that the best method for removing CO_2 and NO_2 is to bubble the product mixture through a 5% aqueous NaOH scrubber. Most of the other impurities, including the nitrogen oxides, can be removed by passing the product through molecular sieves cooled to -78° .

The boiling point of $\text{CF}_3\text{CO}_2\text{NO}$ is 99° ; since it has been found that no significant amount of decarboxylation takes place until a temperature of 145° is reached, it is apparent that this is a vapor phase reaction. Therefore, the production capacity of a decarboxylation unit will be determined by the volume of its vapor chamber. It has been estimated that a five gallon decarboxylation chamber is capable of producing one pound of CF_3NO per hour.

Based upon PCR's previous experience in the production of CF_3NO and upon the information summarized above, the facility for the production of $\text{CF}_3\text{CO}_2\text{NO}$ shown in Figure 4 and the facility for the production of CF_3NO shown in Figure 5 were designed and put into operation. The apparatus shown in Figure 5 was later modified as described below.

Figure 4 shows the $\text{CF}_3\text{CO}_2\text{NO}$ synthesis and storage facility consisting of:

- O O
" "
- A. $\text{CF}_3\text{COCCF}_3$ reservoir
 - B. Transfer lines leading to and from metering pump on opposite side of wall
 - C. Insulated tank housing $\text{CF}_3\text{CO}_2\text{NO}$ synthesis and storage flask.
 - D. N_2O_3 cylinder
 - E. Transfer lines leading through metering pumps on opposite side of wall to pyrolysis flasks
 - F. Coolant circulation pump with lines leading to C and G
 - G. Reflux condenser

In synthesizing $\text{CF}_3\text{CO}_2\text{NO}$, the reaction flask (C) and reflux condenser (G) are first cooled to -20°C by circulating $\text{CCl}_2=\text{CHCl}$. Nitrogen trioxide is then charged into the flask as a liquid. This is followed by the transfer of anhydride from (A) to (C) via a metering pump located on the opposite side of the wall. The facility is designed so that after the N_2O_3 is charged into the flask, all other operations may be carried out remotely. The solution is stirred as the anhydride is added. After addition is completed, stirring is continued as the solution is allowed to warm to 0°C . It is then cooled to -20°C , and a vacuum (~ 1 mm Hg) is pulled on the solution until all unreacted anhydride or nitrogen trioxide has been removed. The flask is then filled with an overgas of N_2 , and the temperature is maintained at $-10 \pm 10^\circ$. The nitrite is transferred through lines (B) by means of the metering pumps (later removed) shown in Figure 5.

Figure 5 shows the CF_3NO production facility as originally installed and which consisted of:

- A. Reservoir of 5% NaOH for wash column, E.
- B. $\text{CF}_3\text{CO}_2\text{NO}$ metering pumps
- C. Two-compartment tank, each side containing a 12-liter flask heated with a mantle and fitted with $\text{CF}_3\text{CO}_2\text{NO}$ inlet and pyrolysis column topped by reflux condenser.

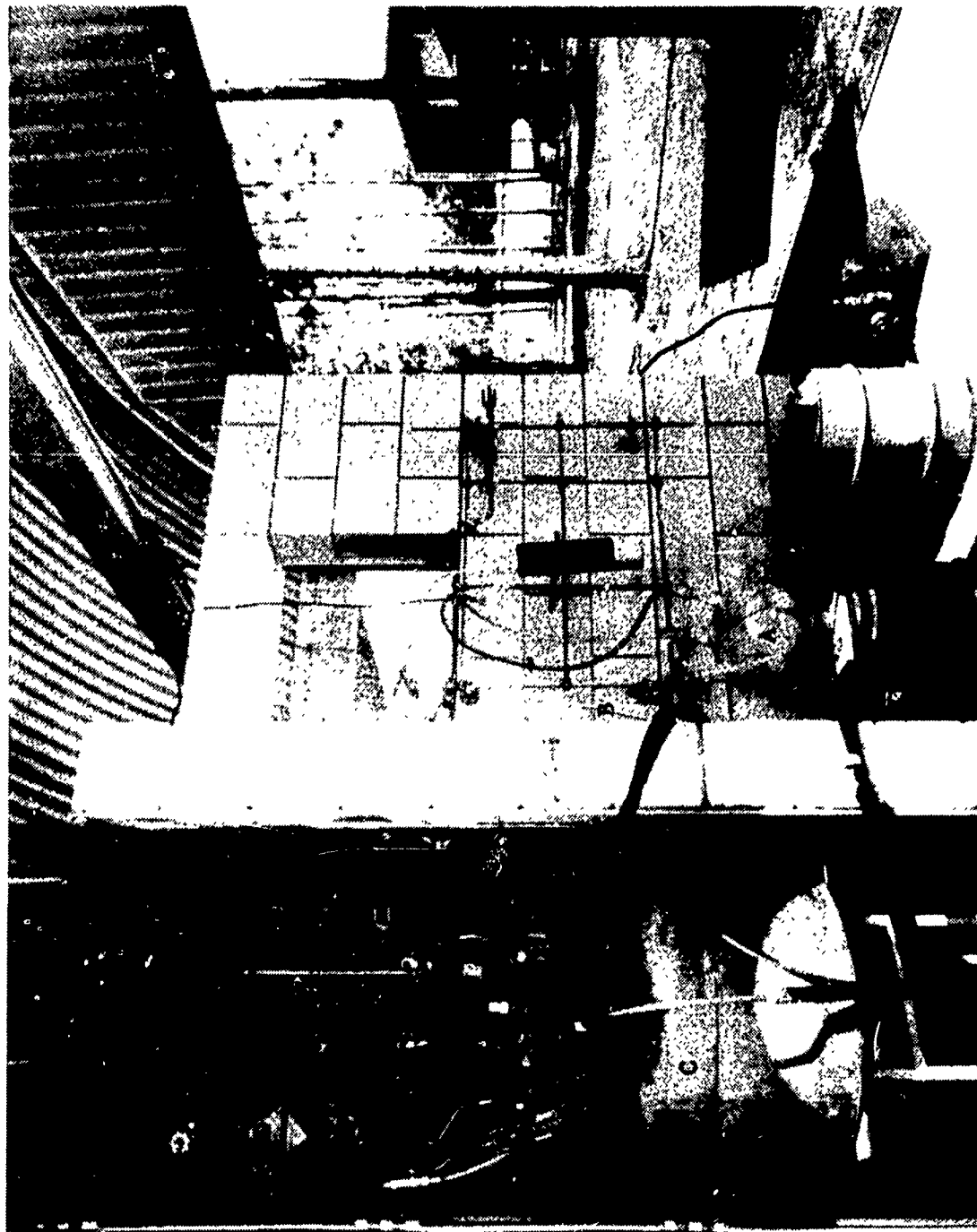


Figure 4. CF_3CONO Production

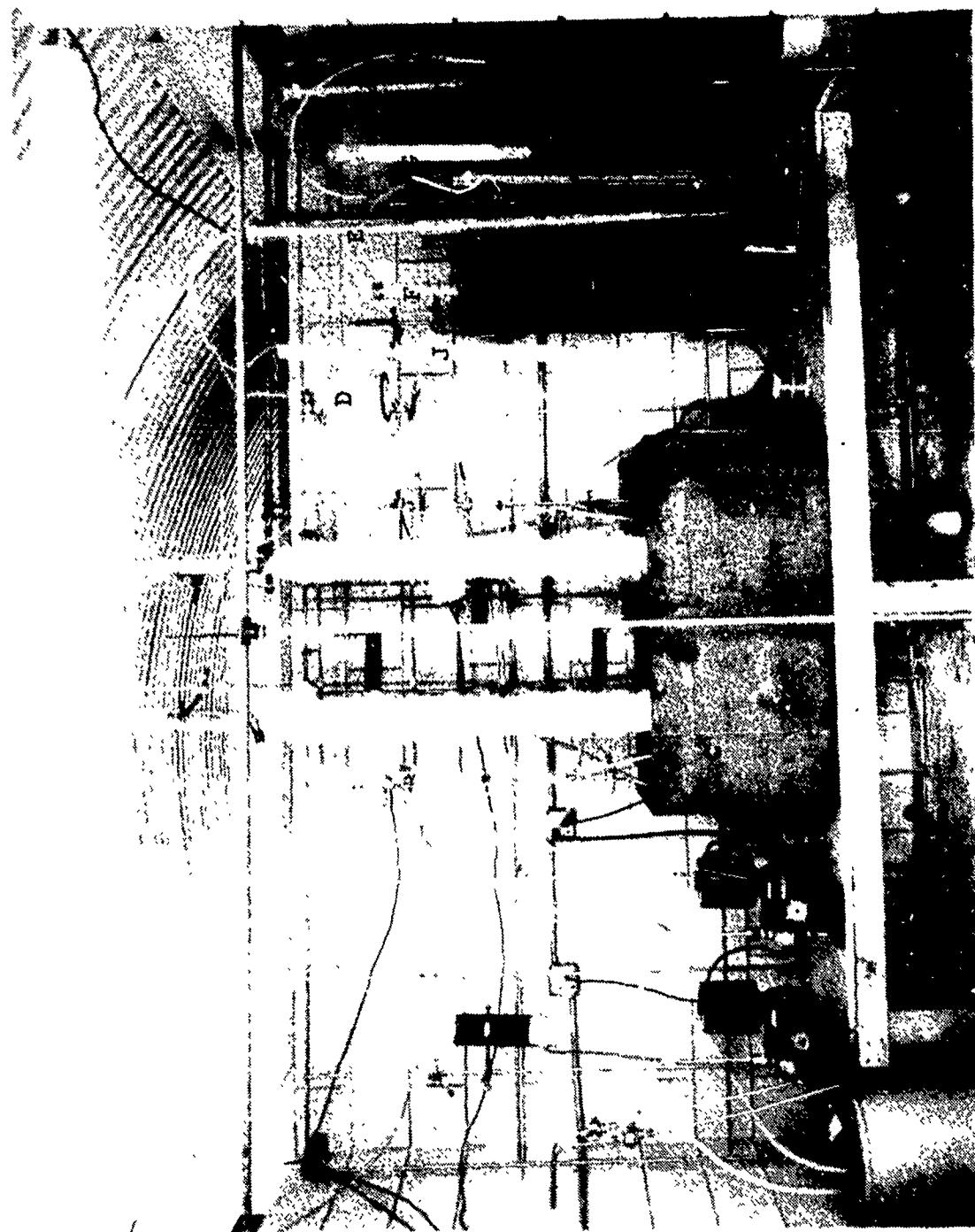


Figure 5. CF₃NO Facility

- D. Air trap as back-up for E
- E. Wash column with circulated 5% NaOH
- F. Glass-packed column cooled to 0°
- G. CaCl₂ drying tube
- H. Molecular sieve-packed column cooled to -78°
- I. Collection flask
- J. Manometers

The pyrolysis columns are 4 in. OD x 4 ft length and have a volume ~2.6 gallons. Each 12-liter flask is charged with 4 liters of FC-43 and has a free volume of ~2.2 gallons.

It was found that the metering pumps would not accurately meter the CF₃COONO. After a considerable effort was expended, these were replaced by pressuring the nitrite through flow meters. However, it was soon found that flow meters would not perform properly for the same reason that the metering pumps wouldn't, that is, the formation of bubbles in the nitrite. Next, the flow meters were replaced with addition funnels. However, this was not satisfactory from a safety stand-point. In the final runs a positive N₂ pressure was maintained on the nitrite as it was bled through stainless steel valves into the decarboxylation flasks. This gave the best control on nitrite rate of addition, but it did not provide for a method of measuring the rate of addition.

During the earlier decarboxylations, stoppages developed in the 5% NaOH wash column. It was observed that this was due to the formation of a clear, colorless solid in the mouth of the gas inlet tube. It was thought that this might be sodium silicate, Na₂O·xSiO₂ (x = 3-5) which is insoluble in Na or K salts but is soluble in water. Consequently, a water scrubber was introduced in the line before the caustic scrubber with the result that there were no subsequent stoppages. The first water scrubber used was made of glass and it was shortly etched through. Glass wool was added to the next scrubber and this succeeded in slowing down the etching process on the glass scrubber until a steel scrubber could be fabricated.

All of the decarboxylations produced a white solid which collected in the reflux condensers. When exposed to air this solid quickly decomposes

to give a brown gas which appears to be NO_2 . Previous work with fluorine compounds in Pyrex has frequently produced a compound which contains Si, F, and NO_2 , and it was supposed that this was the same or a similar compound. It was further thought that this compound reacted with the NaOH in the caustic scrubber to produce sodium silicate. After numerous reactions one of the reflux condensers was cut apart and examined to determine if any etching had taken place. There was a slight frosting of the glass but no measurable etching. On several occasions the pyrolysis flasks and decarboxylation columns were weighed, but no weight loss was observed. Thus it appears that the decarboxylation of CF_3COONO produces materials which readily etch moist glass but are unreactive toward glass under the dry conditions which exist in the decarboxylation chamber.

The last change which was made in the decarboxylation facility was a change in the size of the pyrolysis column. The columns originally designed were 4' x 4'' and were connected by a ball joint to a 12-liter flask. With this size apparatus it was found that CF_3NO could be produced at a maximum rate of just slightly less than 0.5 lb/hr. A new apparatus was fabricated which consisted of a 4' x 6'' column attached to a 12-liter flask. With this apparatus CF_3NO has been produced at the rate of 1 lb/hr. In addition, yields in the 30-40% range were obtained with the smaller apparatus. With the larger column yields in the 50-52% range were obtained. It was thought that these higher yields in the larger column might be due to the more rapid removal of the CF_3NO from the decarboxylation chamber as a result of the faster reaction rates. In order to explore this possibility additional nitrite syntheses and decarboxylations were carried out using both 4'' and 6'' diameter columns. Yields of 46 and 49%, respectively, were obtained, indicating that the yield was not related to column size. In the earlier decarboxylations with the 4'' diameter columns the metering pumps were used. The earlier low yields of CF_3NO are attributed to the frequent shut-downs experienced with these pumps.

E. Phase IV, Thin-Film Polymerization of Carboxy Nitroso Rubber (CNR)

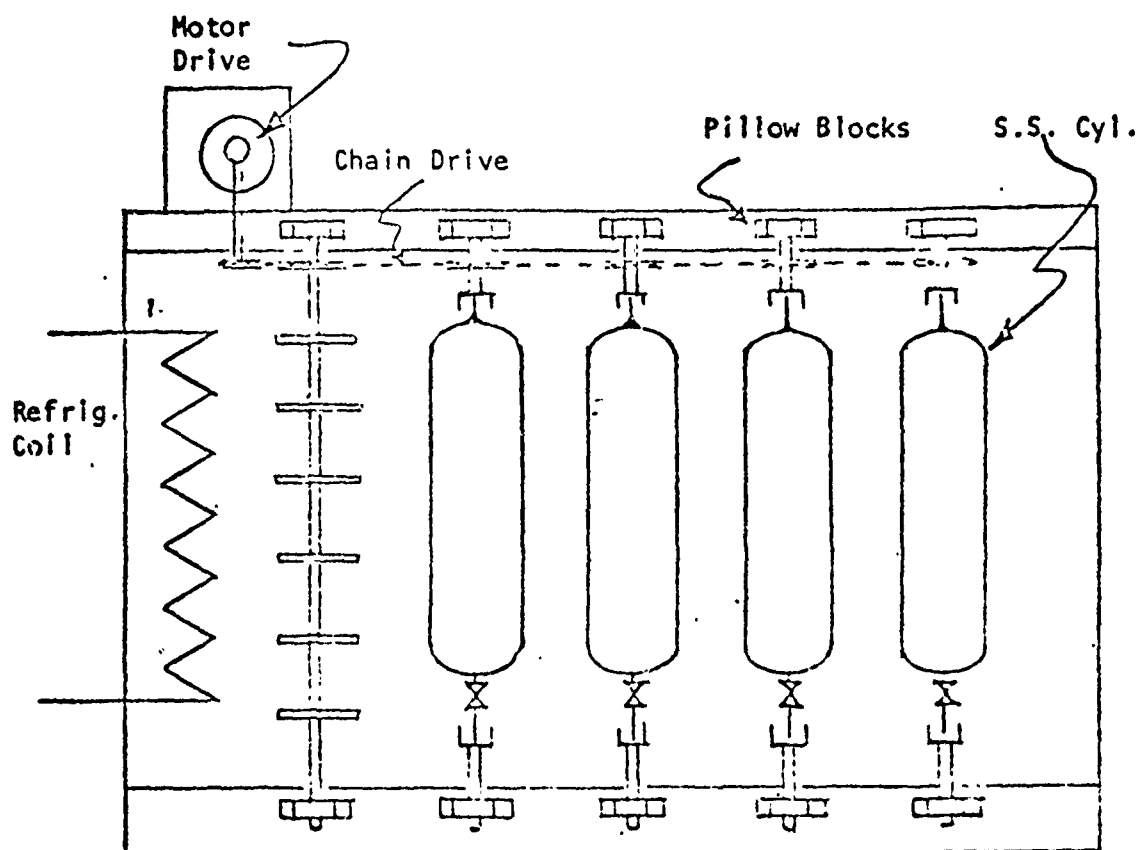
Earlier programs concerned with the large scale production of nitroso rubber and carboxy nitroso rubber have avoided the use of neat (bulk)

polymerizations on the grounds that the heat of polymerization could not be adequately dissipated, in spite of the fact that on a small scale the neat polymerizations gave superior polymers. On the present program it has been demonstrated that the neat polymerization can be scaled up by a 'Thin-Film' polymerization technique. In this process the monomers are charged into metal cylinders which are then rotated about their longitudinal axes in a cold bath. As the polymer is formed it is deposited as a film on the walls of the cylinders. In this way no large amount of insulation is formed between unreacted monomer and coolant, with the result that the heat of polymerization is adequately dissipated.

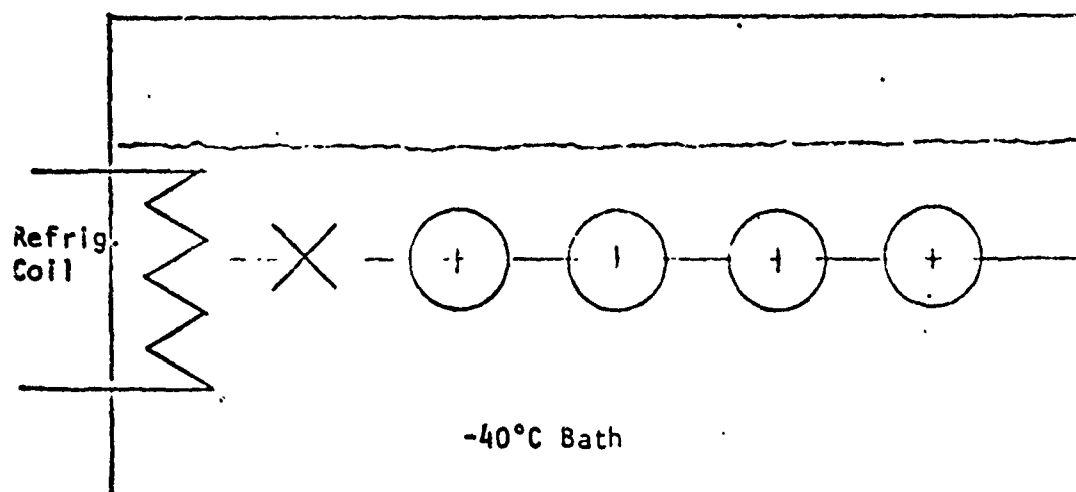
Figure 6 shows a diagram and Figure 7 shows a picture of the polymerization apparatus used on this program. As a result of the corrosion tests shown in Table III, the polymerization cylinders were made of 304 stainless steel. They were 4 inches in diameter by 24 inches in length. Thus, each cylinder had a surface area of $4 \times 2.54 \times 3.14 \times 24 \times 2.54$ or 1945 cm^2 . Assuming that the density of CNR would be the same as nitroso rubber, 1.9 g/cc , and assuming that the polymer would be distributed evenly over the entire surface area of the cylinder, then it was expected that with a 4-lb monomer charge the maximum thickness of polymer on the cylinder wall would be

$$\frac{4 \times 454}{1.9} \div 1945 \text{ or } \sim 0.49 \text{ cm.}$$

The earlier Government-sponsored programs mentioned above had established that the polymerization of CNR may be successfully carried out in the temperature range of -40 to -25°C . The polymerization bath for this program was designed with the idea of maintaining a temperature of -40 to -35° providing the refrigeration unit would handle the heat load under the expected polymerization conditions and a maximum temperature of -25° even if all of the heat of polymerization was delivered instantaneously. It was assumed that the heat of polymerization of CNR is the same as that of nitroso rubber, 75 kcal/mole . Accordingly, it was expected that the polymerization of 16 lb (36.5 moles) of CNR would generate 36.5×75 or 2736 kcal . Since at -40° the specific heat of the bath coolant (Jaysol) is 0.5 cal/g/deg , then to maintain a temperature change from -40 to -25° with the generation of 2736 kcal would require $(2736 \times 10^3) \div (15 \times 0.5)$ or 365 kg of Jaysol.



Top View



Side View

Figure 6. Equipment Diagram - Thin-Film Reactors for Carboxy Nitroso Rubber Production

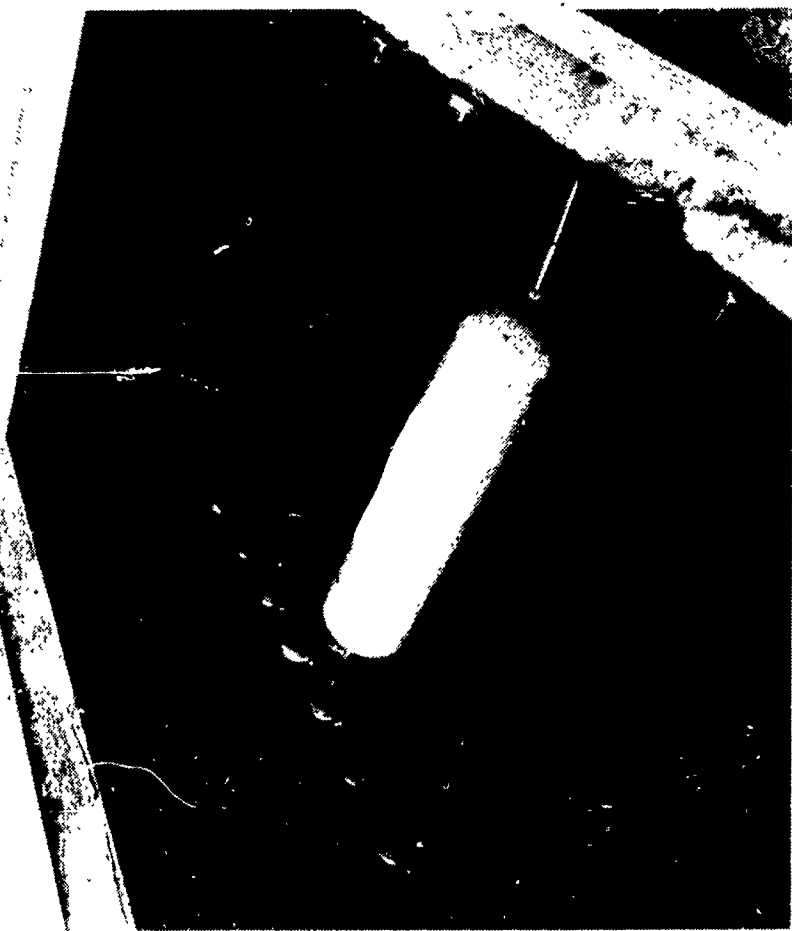
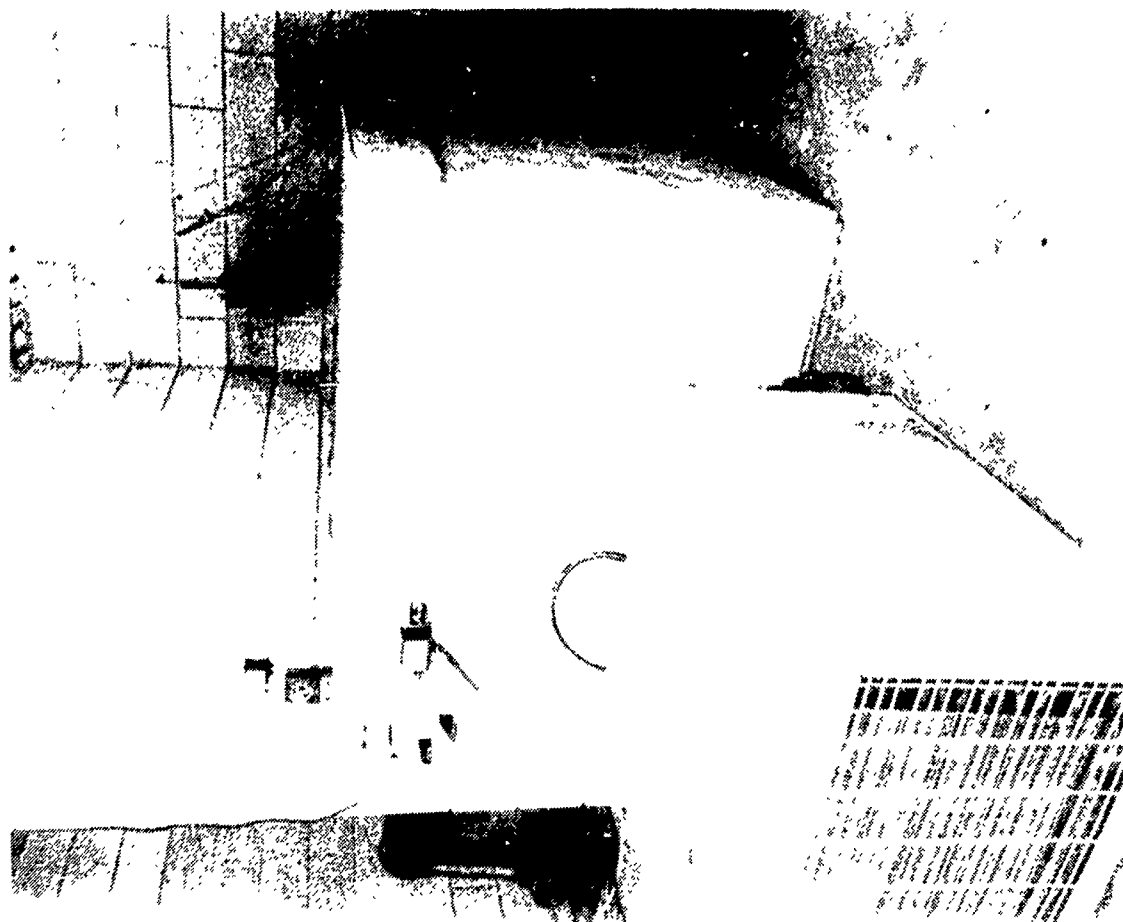


Figure 7. Thin-Film Polymerization Apparatus

TABLE III

CORROSION OF VARIOUS METALS WITH
NITROSPERFLUOROBUTYRIC ACID

Metal	Area (in ²)	Density (g/in ³)	Original Wt. (g)	Final Wt. (g)	NPBA Contact Time (hrs)	Loss (g)	Loss (in ³)	Penetration (in/year)
Carbon steel*								
Copper	0.54	146	1.5704	1.2907	16.5	0.2797	19×10^{-4}	187
Nickel	0.68	127	1.3852	1.1127	60	0.2725	21×10^{-4}	45
304 stainless steel	0.45	132	2.2093	2.2087	68	0.0006	45×10^{-7}	13×10^{-4}
316 stainless steel	0.64	132	1.1848	1.1846	80	0.0002	15×10^{-7}	25×10^{-5}

* A quantitative measurement was not made on the carbon steel, but by visual observation its corrosion rate was more similar to copper than any of the other metals.

Since the density of Jaysol is ~ 0.8 g/cc then 365 kg represents ~ 120 gal. This 120 gal of Jaysol will absorb 2736 kcal while sustaining a temperature change from -40 to -25°C . In actual use the bath was charged with 180 gal of Jaysol.

Two of the monomers used in reaction (1) were synthesized on this program. The third, tetrafluoroethylene, is commercially available as an inhibited material. Before use in the polymerization, the inhibitor (limonene) was removed by bubbling the tetrafluoroethylene through concentrated H_2SO_4 .

After some very small scale polymerizations which were run in glass ampoules as monomer purity checks, a polymerization was carried out in a 4" x 24" cylinder sealed in the middle with a Teflon gasket. A sketch of this cylinder is shown in Figure 8. Prior to use, the cylinder was checked under full vacuum and at 300 psi at both ambient temperature and at -183° with the result that no leaks could be detected. It was then charged with NPBA, cooled to -183° , evacuated, charged with CF_3NO , charged with C_2F_4 , and placed in the polymerization bath. (The system used for charging this and all subsequent polymerization cylinders is shown in Figure 9). After two days it was observed that polymer had been forced out around the Teflon seal. The cylinder was removed from the bath, evacuated and opened. It was found to contain a good polymer, but as material had obviously leaked out it could not be assumed that all of the monomers were present in the desired ratio.

For the second polymerization the flange seals were removed, and the cylinders were welded as one continuous piece. Two of these cylinders were charged as before and again placed into the polymerization bath. In less than 24 hours one of the cylinders ruptured with such violence that the entire polymerization bath was destroyed and the pipe nipple was broken off the second cylinder. Some polymerization had already taken place in the second cylinder at the time that the nipple was broken off. When the cylinder was cut open it was found that all of the polymer was on one side of the cylinder rather than being distributed evenly around the walls.

When these cylinders were placed in the polymerization bath the speed of rotation was adjusted (120 rpm) so that the monomers would not be slung to the walls of the cylinders by centrifugal force but would undergo a tumbling action. It was anticipated that as polymer formed it would adhere to

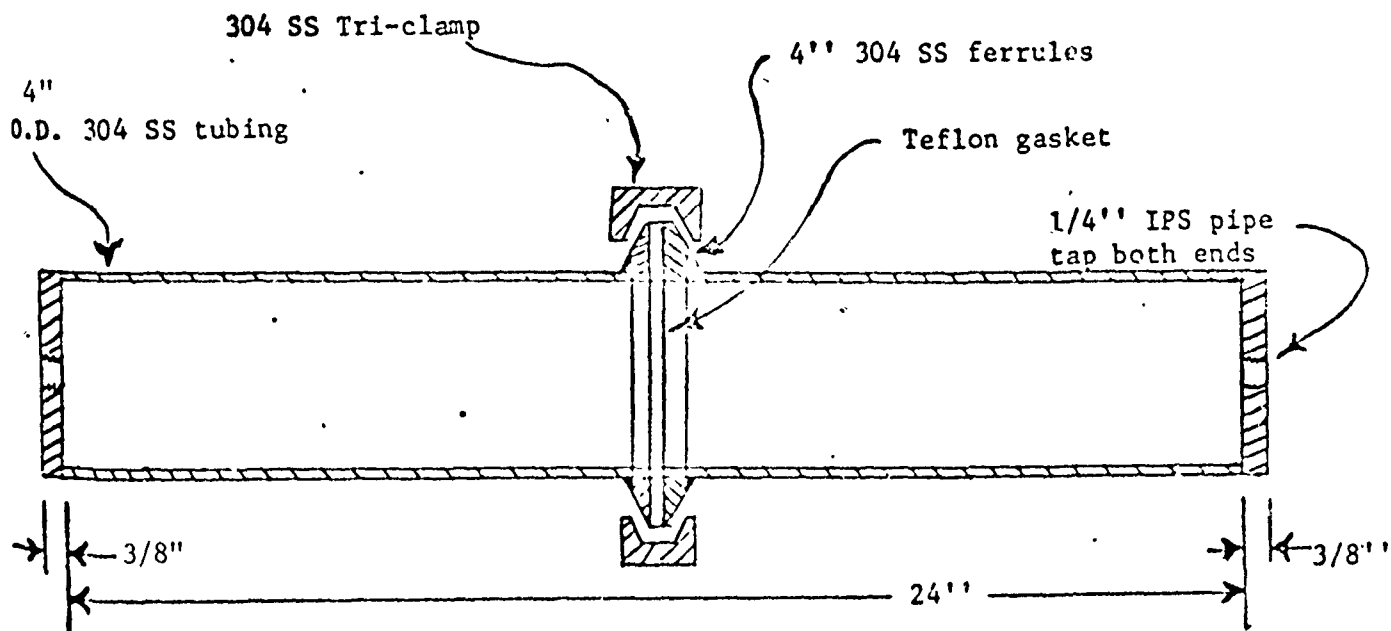


Figure 8. Sketch of Polymerization Cylinder

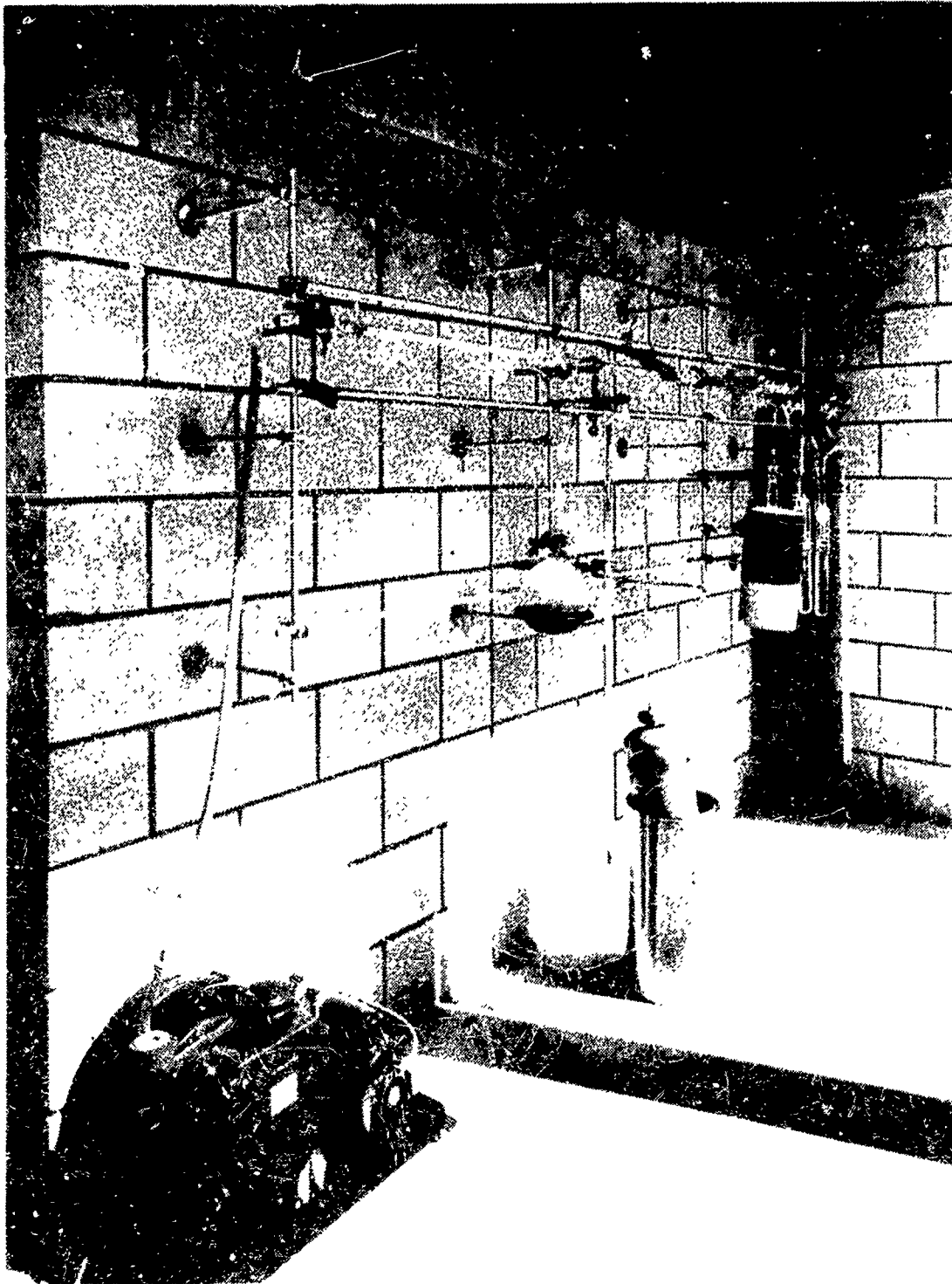


Figure 9. Vacuum System

the walls and in this way form a cylinder of product. In view of the extreme pressure buildup which was experienced and in view of the fact that the polymer was not distributed around the walls, it now appears that the puddling of the monomers caused an almost instantaneous formation of polymer with a resultant instantaneous excess of heat being delivered. This in turn caused the unpolymerized portion of the monomers to react violently. It also appears that the same thing happened to the cylinder sealed with the Teflon gasket, but rather than rupturing the excess pressure caused leakage around the gasket.

Another polymerization bath was built identically to the first one. A single welded cylinder, 4" x 24", was again charged with monomers and placed in the bath. According to the formula $f = 0.0000142n^2d$ where f = force of one gravity, n = number of revolutions per minute, and d = diameter (in inches) of object being rotated, the speed of rotation necessary to overcome the force of gravity, that is, to create a condition whereby the monomers in a 4" diameter cylinder would be distributed about the wall rather than tumbling in the bottom, would have to be greater than $[1 \div (0.0000142 \times 4)]^{1/2}$ or 133 rpm. Consequently, this cylinder was rotated at 180 rpm. After three days the cylinder was degassed and opened; it was observed that a clear, tough gum was deposited evenly around the wall. A 79% conversion was obtained. The low conversion is attributed to mechanical losses in the relatively small-scale run.

Nine subsequent polymerizations were run and a total of 83.9 lb of CNR (1 mole % NPBA) was produced in an average 90% conversion. The only difficulty experienced in these latter runs was the formation of minute specks of what appears to be carbon in the polymer. These carbon particles evidently arise during the process of welding the cylinders. Since the cylinders are heliarc welded with stainless steel rod, a condition which should produce virtually no carbon, it is assumed that the carbon arises from minute particles of CNR trapped in the rough area of former welds. The cylinders are cleaned after each run by a combination of sand-blasting and washing with solvent, but minute traces of CNR apparently still cling to the welded areas.

Some of the CNR obtained from the thin-film polymerizations have been cured at the Air Force Materials Laboratories as follows:

Materials

CNR 100 pph
HiSil EP 20 pph
Chromium trifluoroacetate
5 pph

Curing Conditions

Press cure - 30 min at 250°F
Post cure - 1 hr at 250°F plus 1 hr
at 300°F plus 16 hr at 350°F

This cured material was found to have the following properties:

Tensile	1500 psi
Elongation	165%
Shore A (Hardness)	74 points

The above polymerizations demonstrated that good quality CNR can be made by the thin-film polymerization technique. However, the presence of carbon in the product shows that some type of "gasket" seal must be used on the polymerization cylinders rather than welding them shut.

F. Material Specifications and Safety Precautions

1. Material Specifications

With the exception of C_2F_4 all of the raw materials used on this program were of sufficient purity as purchased from the suppliers (shown in Table VII). All compounds were purchased as reagent grade with the exception of C_5Cl_8 and SbF_5 , these were technical grade materials. As described earlier, tetrafluoroethylene was purified immediately before use.

The intermediates $CF_2CF_2CF_2CCl=CCl$, $ClC(CF_2)_3CCl$, and $O=C(CF_2)_3C=O$ were obtained in sufficient purity (99%) by distillation after synthesis. The intermediates $CCl_2CCl_2CCl_2CCl=CCl$, $HOC(CF_2)_3CONH$, CH_3ONO , $CH_3OC(CF_2)_3CONO$, $CH_3OC(CF_2)_3NO$, and CF_3CONO were used as synthesized, that is, without further purification.

The $HOC(CF_2)_3NO$, synthesized by hydrolysis, was distilled to 96-97% purity and used as such. The only impurity present was $CH_3OC(CF_2)_3NO$. The CF_3NO obtained directly from the production facility was sometimes of sufficient purity (99.9+%) for direct use and sometimes required an additional passage through molecular sieve. The purity of both nitroso monomers was determined by GLC.

The CNR produced should have the minimum following properties when cured as follows:

Ingredients

<u>Compound</u>	<u>PHR</u>
CNR (1 mole % NPBA)	100
Silstone 110	20
Chromium trifluoroacetate	5

Conditions

Press cure (minimum 1000 psi) = 15 min at 250°F

Post cure (circulating air oven) = 1 hr at 250°F, 1 hr at 300°F,
and 16 hr at 350°F

Properties

Tensile strength	1200 psi
Elongation	150 %
Shore A hardenss	75 <u>+5</u> points

2. Safety

The dangers of working with large quantities of H_2SO_4 , NaOH, etc. are well known and need no discussion. The other safety problems connected with the production of CNR are presented below as they arise in reactions (1) - (19).

One of the hazards in reaction (1) was demonstrated dramatically in the pilot plant when insufficient stirring caused the violent reaction of CNR monomers. It is also known that the same violent reaction occurs at temperatures above those employed for polymerization. Therefore, the polymerization must always be carried out in a well barricaded area.

The toxicity of CF_3NO and NPBA has not been established, but it is known that hydrocarbon nitroso compounds can be carcinogenic. These compounds are not explosive but should be treated as toxic. Tetrafluoroethylene is extremely dangerous due to its explosive tendencies in a purified state. It has been established that a detonation is likely any time the compound

is subject to pressures above 40 psi at ambient temperature. The dangers involved in working with C_2F_4 are well documented and a review of the literature⁸ should be undertaken before the material is handled in any manner. The main safety hazard in reaction (4a) is that of working with SbF_5 . Contact with this material can cause severe HF burns. The pilot plant production of $ClC(CF_2)_3C(=O)Cl$ was always accompanied by the odor of phosgene when the material was removed from the reactor. On the smaller scale this presented no particular problem, but it should be considered as a possible source of toxic gas when manufactured on a production scale. The product of reaction (7), perfluoroglutaric anhydride, also produces a very sharp and suffocating vapor. Again, studies are not available on this compound, but it should be treated as toxic.

No problem has been experienced with CMPBN produced in reaction (8), but it was always treated as a potentially dangerous compound. In general, nitrites tend to be explosive and this material has always been handled as a potentially explosive compound. Again, even though no explosions were experienced in the pilot plant and none have been reported by previous workers, the material should be handled with caution until studies of its properties have been investigated. The properties of CH_3ONO prepared in reaction (19) and used in reaction (8) are described in the literature.⁹

Although no pilot plant problems were experienced with reactions (11) and (12) in the production of CF_3NO , they were treated with extreme caution. Earlier workers^{4,7} have reported explosions both in the decarboxylation chambers and in nitrite reservoirs. These problems have apparently been eliminated through the use of FC-43 as a diluent in the decarboxylation, but, again, since large quantities of a nitrite are to be handled, it must be well barricaded. Also, personnel must be shielded from the decarboxylation chambers.

G. Phase V, Evaluation and Projected Scale-up of Pilot Plant

1. Projection of Pilot Plant to Manufacturing Facility

It now appears that all of the reactions utilized in the final Pilot Plant demonstrations for the synthesis of CNR monomers and their intermediates

can be scaled up to production capacity. These scale-ups should involve nothing more than the use of larger equipment, with the normal considerations of larger heat reservoirs, larger weights of equipment and materials, more time for reactions, greater danger from hazardous reactions, etc. In other words, for monomer synthesis there should be no need to employ techniques or rely upon engineering novel to the pilot plant facility.

As an example of the above, in the pilot plant the oxidation of $\text{CF}_2\text{CF}_2\text{CF}_2\text{CCl}=\text{CCl}$ was carried out in a single 22-liter flask; in the production plant it is proposed to carry out this reaction in ten 72-liter flasks. In the pilot plant the pyrolysis of $\text{CH}_3\text{OC}(\text{CF}_2)_3\text{CONO}$ was carried out in a 500-ml flask with an 18" column; in the production facility two 12-liter flasks with 6" x 48" columns are proposed. In the pilot plant a single 12-liter flask with a 6" x 48" column was used for CF_3NO production; for the production facility seven such set-ups are proposed. In a similar manner it is proposed to simply use larger equipment for fluorinations, hydrolyses, dehydrations, etc.

Contrary to the above, the polymerization reaction will require somewhat different techniques on the 100,000 lb/yr production level than it did on the pilot plant level. It is proposed to carry out the polymerization in 4" diameter cylinders in the production facility as they were in the pilot plant, but new methods of cooling, charging, and handling must be employed. In the pilot plant individual cylinders were evacuated, cooled in liquid air, and charged with NPBA by pouring this compound into a funnel attached to the cylinder and then cracking the cylinder valve until all of the liquid was drawn in. The cylinder was then evacuated again and CF_3NO was volatilized from a storage cylinder through a vacuum manifold into the polymerization cylinder. This was followed by the transfer of C_2F_4 to the polymerization cylinder in a similar manner. The cylinder valve was then closed and the cylinder was manually transferred to the -40° polymerization bath. The loading of one cylinder required one and one-half hours and consumed a considerable quantity of liquid air.

If a similar technique were employed on a 100,000 lb/yr production scale, cylinder loading time alone would require almost 40,000 hours. Aside from this the cost of liquid air would be prohibitive. Finally, the danger involved in exposing personnel to the handling of thousands of polymerization cylinders puts the pilot plant technique out of the question for production work.

It is proposed that for a production plant racks should be built which would support fifteen 4" x 24" cylinders in gear-driven bearings. For loading purposes a rack would be placed upright in a -78° bath with only the vented ends of the cylinders exposed. Monomers would then be charged to the cylinders through an automatic feed line which allows transfer of CF_3NO and C_2F_4 at -78° under a slight pressure. After the cylinders are charged an automatic crane would lift the rack from the -78° bath and transfer it to a -40° polymerization bath. The act of the crane setting the rack of cylinders in place would engage gears which would rotate the cylinders. A facility housing fifteen baths which would each accomodate a rack of fifteen cylinders would be sufficient to produce 100,000 lb of CNR on a twenty-four hour a day basis.

2. Summation of Projected Synthesis and Cost

Based on the information generated on this and earlier programs, it is now projected that Carboxy Nitroso Rubber containing 1 mole % nitroso-perfluorobutyric acid can be manufactured at the rate of 100,000 lb/year at a cost of \$44.73/lb. This can be done by utilizing the proven reactions (1), (3), (4a), (5), (6), (7), (8), (9), (10), (11), (12), (16), (18), and (19). The established yields and products from these reactions are shown in Table IV.

For the purpose of evaluation the total CNR manufacturing cost has been broken down into Buildings, Equipment, Material, Labor, and Overhead. The annual cost of these items is summarized in Table V. The total cost under each heading is rounded to the nearest one hundred dollars.

In projecting the cost for the proposed manufacturing program there is an obvious relationship between equipment costs and labor costs. For

example, in considering reaction (4a), the fluorination of C_5Cl_8 with SbF_5 , the labor cost is necessarily related to the number of times which the reaction must be carried out. This, in turn, is dependent upon the size of the reaction kettle used. In each step of the proposed program it was necessary to consider this relationship between labor and equipment. Rather than present all of the various possibilities which were considered, only the cost estimate based upon the most practical compromise between the two is presented. Figure 10 shows a flow diagram for the proposed 100,000 lb/year CNR plant.

TABLE IV

PER CENT YIELD OF PRODUCTS FROM REACTIONS (1) - (12) and (19)

<u>Reaction No.</u>	<u>Product</u>	<u>% Yield</u>
1	CNR	90
2	SbF ₃ Cl ₂	
3	$\overline{\text{CCl}_2\text{CCl}_2\text{CCl}_2\text{CCl}=\text{CCl}}$	100
4a	$\overline{\text{CF}_2\text{CF}_2\text{CF}_2\text{CCl}=\text{CCl}}$	80
5	$\begin{array}{c} \text{O} \quad \text{O} \\ \quad \\ \text{ClC}(\text{CF}_2)_3\text{CCl} \end{array}$	95
6	HOOC(CF ₂) ₃ COOH	100
7	$\begin{array}{c} \text{O} \\ / \quad \backslash \\ \text{O}=\text{C}(\text{CF}_2)_3\text{C}=\text{O} \end{array}$	95
8	$\begin{array}{c} \text{O} \quad \text{O} \\ \quad \\ \text{CH}_3\text{OC}(\text{CF}_2)_3\text{CONO} \end{array}$	100
9	$\begin{array}{c} \text{O} \\ \\ \text{CH}_3\text{OC}(\text{CF}_2)_3\text{NO} \end{array}$	45
10	$\begin{array}{c} \text{O} \\ \\ \text{HOC}(\text{CF}_2)_3\text{NO} \end{array}$	90
11	$\begin{array}{c} \text{O} \\ \\ \text{CF}_3\text{CONO} \end{array}$	100
12	CF ₃ NO	50
19	CH ₃ ONO	85

TABLE V

BREAKDOWN OF ANNUAL COST OF CNR MANUFACTURING PROGRAM

Buildings	\$ 31,100
Equipment	182,400
Materials	2,239,900
Labor	380,100
Overhead	<u>1,639,200</u>
<u>Total</u>	<u>\$4,472,700</u>

3. Buildings

Figures 11 and 12 show floor plan sketches for two buildings which would be required for CNR production. These sketches were not made to place the various items of equipment in specific locations but to estimate the amount of floor space required for the manufacturing program. In actual construction it may be desirable to erect more than two buildings so that some of the more hazardous operations can be isolated. However, the total required floor space would be approximately the same, and the cost may be estimated as if the two buildings were to be utilized.

In Figure 11 it is seen that the Intermediate Synthesis building covers 5850 sq ft, and in Figure 12 the Polymerization building covers 7650 sq ft. The annual cost for these buildings may be estimated as follows:

$$\text{Annual Cost} = \frac{(\text{square footage}) \times (\text{cost per square foot})}{(\text{number of years depreciated})}$$

Assuming a cost of \$20.00/sq ft and a depreciation period of 10 years, then:

Annual cost of Intermediate Synthesis Building =	$\frac{(5850) \times (20.00)}{10} =$	\$11,700
Annual cost of Polymerization Building =	$\frac{(7650) \times (20.00)}{10} =$	15,300
Sub-total =		27,000
Contingency at 15% =		4,050
Total Annual Building Cost =		\$31,100

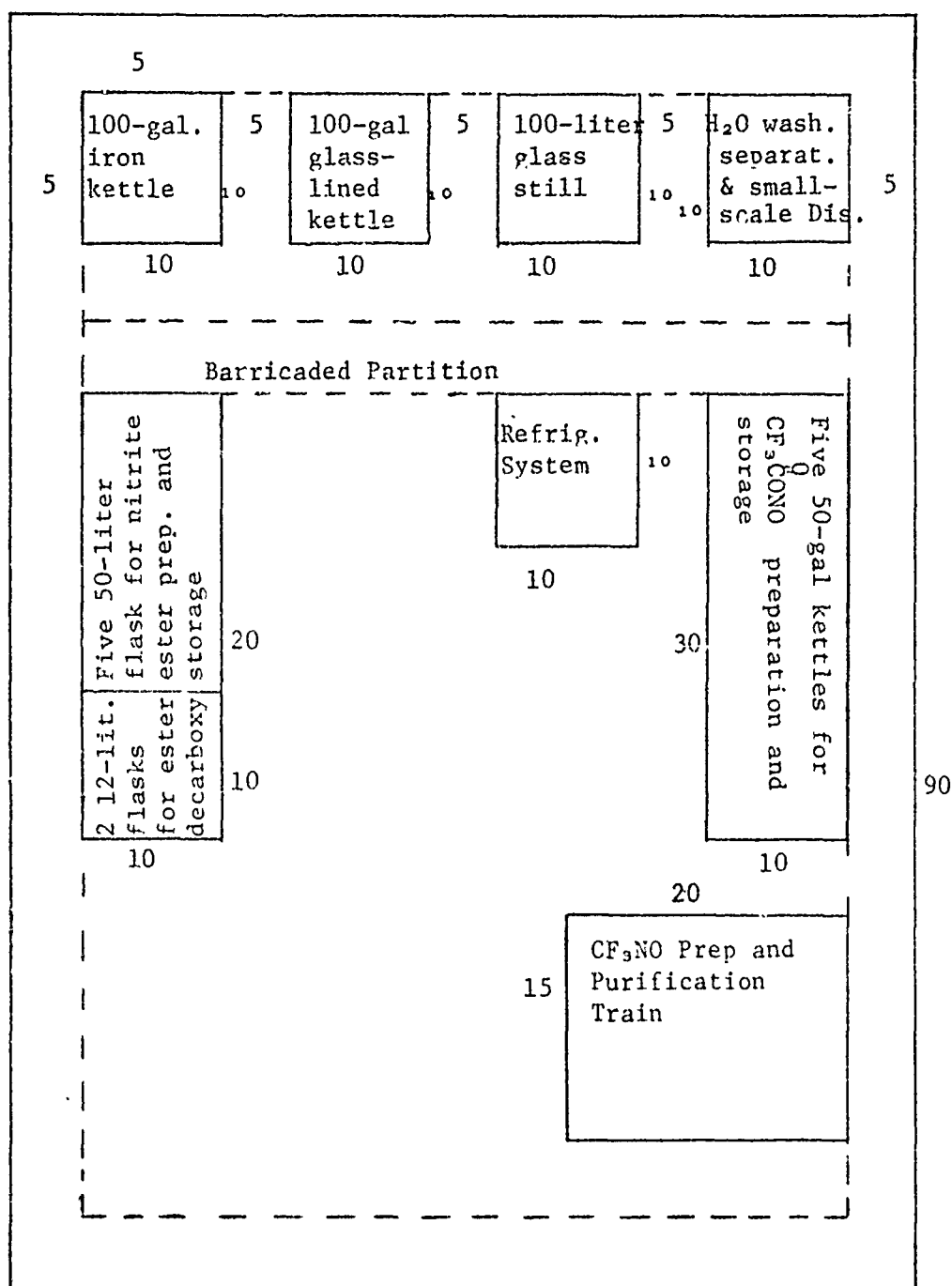


Figure 11. INTERMEDIATE SYNTHESIS BUILDING FLOOR PLAN

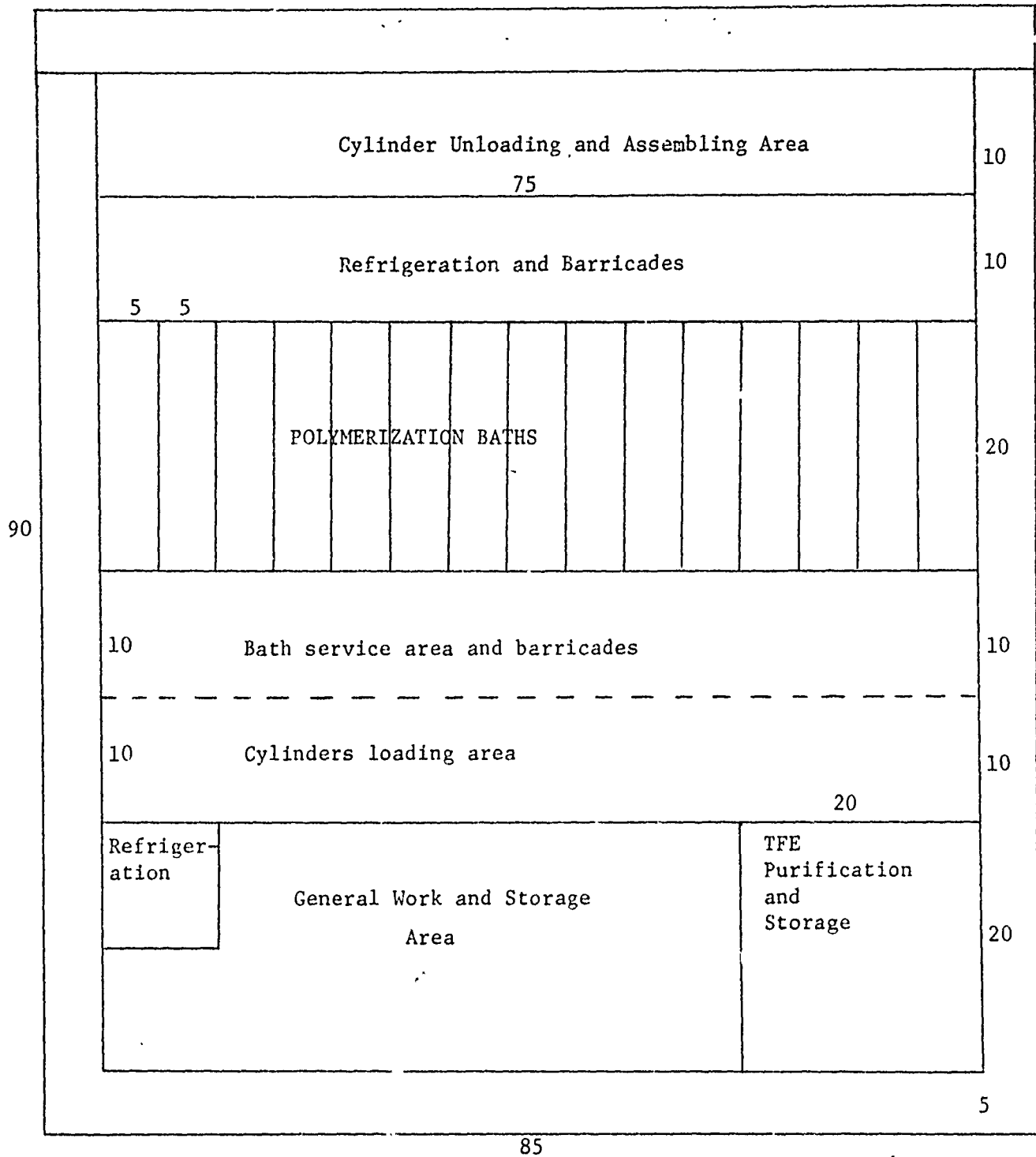


Figure 12. POLYMERIZATION BUILDING FLOOR PLAN

4. Equipment

The various items of equipment and their estimated costs are shown in Table VI. Assuming that the equipment will be depreciated over a five-year period, the annual equipment cost may be estimated as follows:

Equipment cost from Table VI =	\$793,200
Contingency at 15% =	118,900
Total Cost =	912,100
Annual Cost =	182,400

5. Materials

The annual material requirement for the proposed manufacturing program is shown in Table VII. With the 15% contingency allowance the total annual material cost is estimated to be:

Sub-total Material Cost from Table VII =	\$1,947,740
Contingency at 15% =	292,160
Total Annual Material Cost =	2,239,900

6. Labor

From Table VIII it is seen that the annual labor requirement is 61,974 technician hours and 2076 supervisor hours. Assuming a wage of \$5.00/hr for a technician and \$10.00/hr for a supervisor, the annual labor costs are estimated as:

Cost of Technicians = $61,974 \times \$5.00$ =	\$ 309,870
Cost of Supervisor = $2,076 \times \$10.00$ =	20,760
Sub-total =	330,530
Contingency at 15% =	49,580
Total Annual Labor Cost =	\$ 380,100

TABLE VI

EQUIPMENT

<u>Quantity</u>	<u>Item</u>	<u>Use</u>	<u>Installed Cost</u>
1	100-gal iron kettle with all accessories	Reactions (3) and (4a)	\$8,000
1	100-gal glass-lined kettle with all accessories	Reactions (6), (7), (10), & (19)	15,000
10	72-liter flasks	Reaction (5)	2,000
5	50-liter flask & heating mantle	Reaction (8)	1,400
9	12-liter flask with 6 x 48" neck and heating mantle	Reactions (9) & (12)	2,300
27	Reflux condensers	Reactions (9) & (12)	1,300
24	CF ₃ NO purification train with accessories	CF ₃ NO Purification	7,200
1	100-liter glass still	Purification of intermediates	3,000
5	50-gal stainless steel kettle with accessories	Reaction (11)	60,000
	Miscellaneous glassware		3,000
	Miscellaneous work benches, pumps, gauges, etc.		10,000
1	Acid storage and neutralization tank	Neutralize excess H ₂ SO ₄ from reaction (10)	10,000
1	TFE purification and storage facility with accessories	Purification of TFE prior to polymerization	30,000
15	Polymerization tank	Reaction (1)	30,000
15	Polymerization rack	Reaction (1)	15,000
250	Polymerization cylinder	Reaction (1)	125,000
1	Polymerization loading facility	Reaction (1)	30,000
2	Refrigeration system	Reaction (1)	100,000
1	Automated transport system	Transferring cylinder from loading area to polymerization bath to unloading area	300,000
1	Refrigeration system	Intermediate synthesis building	40,000

TOTAL

\$793,200

TABLE VII

MATERIALS REQUIRED FOR PRODUCTION OF 100,000 LB OF CNR (1 MOLE % NPBA)

Compound	Materials Source	Amount (lb)	Amount (gal)	Unit Cost (\$/lb)	Sub-total (\$)	Shipping Cost (\$)	Total (\$)
SbF ₅	Allied	15,545	622	14.00	217,630	777	218,407
$\text{CCl}=\text{CClCCl}_2\text{CCl}=\text{CCl}$	Hooker	10,864	765	0.2375	2,580	543	3,123
Cl ₂	Ace	3,000	148	0.14	420		420
$\text{CCl}_2\text{CCl}_2\text{CCl}_2\text{CCl}=\text{CCl}$	Reaction (3)	13,690	913				
$\text{CF}_2\text{CF}_2\text{CF}_2\text{CCl}=\text{CCl}$	Reaction (4)	7,800	586				
$\text{ClC}(\text{CF}_2)_3\text{CCl}$	Reaction (5)	8,378	644				
$\text{HOC}(\text{CF}_2)_3\text{COH}$	Reaction (6)	7,259	558				
P ₂ O ₅	Stauffer	7,259		0.20	1,452	263	1,715
$\text{O}=\text{C}(\text{CF}_2)_3\text{C}=\text{O}$	Reaction (7)	6,043	465				
CH ₃ ONO	Reaction (19)	1,661	~130				
$\text{CH}_3\text{OC}(\text{CF}_2)_3\text{CONO}$	Reaction (8)	7,704	593				
$\text{CH}_3\text{OC}(\text{CF}_2)_3\text{NO}$	Reaction (9)	2,928	225				
H ₂ SO ₄	Corco	45,490	2,980	0.1275	5,800	2,275	8,075
$\text{HOC}(\text{CF}_2)_3\text{NO}$	Reaction (10)	2,481	191				
CF ₂ =CF ₂	Thiokol	55,137		16.00	882,192	2,757	884,949
CF ₃ NO	Reaction (12)	53,493					
NaNO ₂	Ross	2,211	138	0.16	354		354
CH ₃ OH	Fisher	1,025	154	0.221	227		227
$\text{CF}_3\text{COC}(\text{CF}_2)_3\text{CF}_3$	Halocarbon	113,470	8,728	6.00	680,820	5,674	686,494
N ₂ O ₃	Air Products	41,065		1.50	61,598	2,053	63,651
$\text{CF}_3\text{COC}(\text{CF}_2)_3\text{NO}$	Reaction (11)	154,535	11,887				
CF ₃ CO ₂ H	3M	6,121		11.60	71,004	306	71,310

TABLE VII (Cont.)

<u>Compound</u>	<u>Materials Source</u>	<u>Amount</u>		<u>Unit</u>	<u>Sub-total</u>	<u>Shipping</u>	<u>Total (\$)</u>
		<u>(lb)</u>	<u>(gal)</u>	<u>Cost (\$/lb)</u>		<u>Cost (\$)</u>	
Fomblin	Montecatini-Edison	82		40.00	3,280		3,280
NaOH	Ross	47,794		0.12	5,735		5,735
					\$1,933,092	\$14,648	\$1,947,740

TABLE VIII
LABOR FOR CNR MANUFACTURING PLANT

<u>Operation</u>	<u>Number of Personnel</u>	<u>Type</u>	<u>Schedule</u>	<u>Time (hrs)</u>
Reactions (3) & (4a)	1	Technician	8 hr/day, 2 months	346
Purify C ₅ F ₆ Cl ₂	1	"	" "	346
Reaction (5)	1	"	" "	346
Reactions (6) & (7)	1	"	" "	346
Reaction (19)	1	"	" 1 month	173
Reaction (8)	1	"	" 3 months	519
Reaction (10)	1	"	" 2 months	346
Reactions (9), (11) & (12)	3	"	24 hr/day with 3 men/ shift for 330 days	23,700
TFE Purification & Reaction (1)	4	"	24 hr/day with 4 men/ shift for 330 days	31,700
Misc. distillations & assisting operations	2	"	8 hr/day for 12 months	4,152
TOTAL				61,974
Supervise Operation of Plant	1	Supervisor	8 hr/day for 12 months	2,076

7. Overhead

Since the estimated equipment costs are presented as installed costs, overhead includes no installation costs. It does, however, include everything else that is not specifically listed above. For example, overhead takes in repairs and maintenance, analysis, office and clerical work, taxes, insurance, utilities, fringe benefits, etc. Based on the current overhead rate at PCR, this cost is calculated as follows:

$$(\text{direct labor cost}) \times (3.75) = \text{overhead expenses}$$

For the CNR manufacturing program

Overhead = 380,100 x 3.75 =	\$1,425,375
Contingency at 15% =	213,806
Total Annual Overhead =	1,639,200

III. CONCLUSIONS AND RECOMMENDATIONS

This program has demonstrated the feasibility of producing CNR on a large scale utilizing the thin-film polymerization technique. In the event that a production plant is to be established it is recommended that it be preceded by a pilot plant to consider the following:

1. It is believed that the cost of CNR could be reduced by ~\$0.75/lb by developing the technique of regenerating antimony fluorides with HF for the fluorination of perchlorocyclopentene.

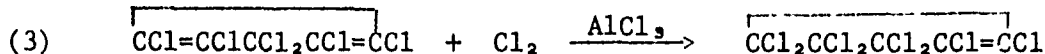
2. The techniques used in handling the polymerization cylinders on the present program are not those which could be recommended for a production facility. Different techniques and different polymerization cylinders should be utilized on another pilot plant level.

In addition to the above, it should be pointed out that any future consideration for the reduction of the cost of CNR should include exploring the possibility of replacing trifluoronitrosomethane with a less expensive monomer.

IV. EXPERIMENTAL

A. Phases I and II, Production of PFGA and NPBA

1. Chlorination of Perchlorocyclopentadiene

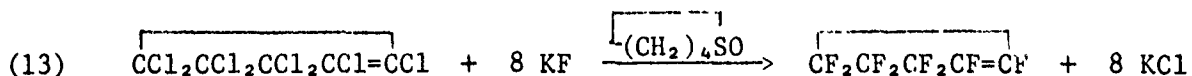


Perchlorocyclopentadiene was chlorinated several times, with the yield of perchlorocyclopentene consistently being above 98%. The following represents a typical run.

Hexachlorocyclopentadiene (1,638 g, 6 moles), AlCl_3 (30 g) and a stirring bar were put into a 3-liter flask fitted with a thermometer, low-temperature reflux condenser, and a gas inlet valve connected to a cylinder of chlorine. The mixture was stirred rapidly as Cl_2 was bubbled in at a rate of ~ 200 g/hr. The reaction was exothermic but easily controlled with an ice bath. After the addition of 500 g (7 moles) of Cl_2 the reaction was stopped. The product was washed with 2.5 liters of warm H_2O and the organic layer which separated was dried in a vacuum oven to give the crystalline $\overline{\text{CCl}_2\text{CCl}_2\text{CCl}_2\text{CCl}=\text{CCl}}$ weighing 2,000 g (98.5% yield). An analysis for carbon gave: found, 17.5%; theory, 17.5%.

2. Fluorination of Perchlorocyclopentene and Perchlorocyclopentadiene

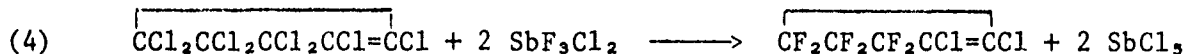
a. Fluorination of Perchlorocyclopentene with Potassium Fluoride



Several reactions of KF with $\overline{\text{CCl}_2\text{CCl}_2\text{CCl}_2\text{CCl}=\text{CCl}}$ were carried out to give $\sim 80\%$ yields of $\overline{\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}=\text{CF}}$. The following describes a typical reaction.

Potassium fluoride (850 g, 14.7 mole) was put into a 5-liter flask fitted with a mechanical stirrer, thermometer, reflux condenser, and dropping funnel; the flask was heated to 200° under full vacuum for 20 hrs. This was followed by the addition of dry sulfolane (800 ml) which resulted in a slurry of KF. While the mixture was heated at 200°, perchlorocyclopentene (367 g, 1.06 mole or 8.5 mole of Cl) was added through the addition funnel over a 3 hr period. The reflux condenser was vented through a 0° trap where perfluorocyclopentene (171 g, 0.81 mole) was collected as the C₅Cl₈ was added to the reaction mixture. The product was 97.5% pure by GLC, representing an 80% yield. Distillation of the pot residue gave 650 ml of sulfolane (81% recovery).

b. Fluorination of Perchlorocyclopentene with Antimony Pentachloride/Hydrogen Fluoride



Fluorinations of C₅Cl₈ with SbCl₅/HF were carried out in a 25-gal iron kettle. Since the yields of C₅F₈Cl₂ were low, the reaction was scaled down to a 1-gal kettle as a means of saving time while attempting to establish better conditions. However, the product yield was not increased in the smaller kettle so the SbCl₅/HF fluorinations were abandoned in favor of SbF₅ fluorinations. The following describes several of the SbCl₅/HF fluorinations.

Antimony pentachloride (12,770 g, 42.7 mole) from PCR stock was analyzed and found to contain <1% Sb³⁺. This material was put into the 25-gallon fluorination kettle. Anhydrous HF (2270 g, 113.5 moles) was added over a 5-hr period as the mixture was maintained at near ambient temperature. After the HF addition was completed the mixture was heated at 80° for 18 hrs. This was followed by the addition of $\overline{\text{CCl}_2\text{CCl}_2\text{CCl}_2\text{CCl}=\text{CCl}}$ (8809 g, 25.6 moles) which was melted (mp 38°) and added as rapidly as possible through an addition funnel. The kettle was then heated for 24 hrs at 80°. The reaction kettle was then fitted with a strip condenser and the temperature was raised to ~180° before product began distilling off. The product was caught as a mixture of solid and liquid weighing 8591 g. An infrared spectrum showed the liquid to be a mixture of partially fluorinated cyclopentenenes. Analysis of the solid showed it to contain <1% Sb³⁺.

The kettle was disassembled and all of the residue from the previous reaction was removed. It was reassembled and charged with SbCl_5 (12,952 g, 43.3 moles) containing <1% Sb^{3+} and C_5Cl_8 (5938 g, 17.3 moles). These materials were stirred at ambient temperature as HF (7264 g, 363.2 moles) was added during a 4-hr period. After the addition of HF, the mixture was heated at 85° for 18 hrs. The mixture was then heated to 175° and strip distilled to give 2900 g of liquid along with some solids. The distillation was stopped when the ratio of solid to liquid became appreciable. The liquid product was washed with 3 liters of 1:1 HCl followed by washing with H_2O ; it was then dried over CaSO_4 , filtered, and distilled to give two fractions containing $\text{CF}_2\text{CF}_2\text{CF}_2\text{CCl}=\text{CCl}$. The first fraction (bp = 88-92°, 93% by GLC) weighed 1028 g, and the second fraction (bp = 95-102°, 84% by GLC) weighed 111 g. This represents a 25% conversion to $\text{CF}_2\text{CF}_2\text{CF}_2\text{CCl}=\text{CCl}$. The pot residue was shown by infrared spectrum to be a mixture of partially fluorinated cyclopentenes.

Enough SbCl_5 was added to the residue from the above fluorination to give a total of 43,600 g (145.8 mole) of SbCl_5 (<1% Sb^{3+}). To this was added C_5Cl_8 (19,904 g, 57.86 moles) and the mixture was stirred. For this reaction the HF addition tube opened beneath the surface of the reaction mixture. Anhydrous HF (12,485 g, 624.3 moles) was added over a six-hour period as the pot temperature was maintained at 35-40°. After the HF addition was completed, the mixture was stirred at 100° for 68 hrs. It was then strip distilled as before to give a mixture of solid and liquid. A portion of the liquid product was washed with 1:1 HCl, water, dried over CaSO_4 , filtered, and distilled. However, when a pot temperature of 130° was reached with no indication of boiling, the entire mixture stripped from the reaction kettle was returned to the kettle for further reaction. An additional 4313 g (215.7 moles) of HF was added over a six-hour period. The mixture was then heated at 135° for an additional 68 hrs. Strip distillation again gave a mixture of solid and liquid. Analysis of the solid showed <1% Sb^{3+} . When this material was dissolved in dilute HCl only a very small organic layer separated. The liquid obtained from the distillation was decanted from the solid, washed with 1:1 HCl, washed with H_2O , dried over CaSO_4 , filtered, and weighed to give 10,710 g of a clear, light-yellow product. This material was distilled to give five fractions containing $\text{CF}_2\text{CF}_2\text{CF}_2\text{CCl}=\text{CCl}$:

<u>Fraction No.</u>	<u>Weight</u>	<u>b.p.</u>	<u>% C₅F₆Cl₂ by GLC</u>
1	1446 g	89-93°	90
2	276 g	95°	92
3	536 g	93-95°	93
4	638 g	95-104°	85
5	338 g	104-120°	67

This represents a 20% conversion to $\overline{\text{CF}_2\text{CF}_2\text{CF}_2\text{CCl}=\text{CCl}}$.

In another reaction the 25 gal kettle was charged with SbCl₃ (109 lb, 165.5 moles) and C₅Cl₈ (52 lb, 68.6 moles) and the addition of HF was begun. After about 30 minutes of HF addition the line to the HF dip tube broke and a considerable quantity of material was pressured out of the kettle before it could be brought under control. The material remaining in the kettle was transferred to a tared container, found to weigh 99.5 lb, and then transferred back to the kettle. Assuming that the lost material was a homogenous solution of C₅Cl₈ in SbCl₃, this left 67.4 lb (102 moles) of SbCl₃ and 32.1 lb (42.4 moles) of C₅Cl₈ in the kettle.

During a 4-hr period HF (9.0 lb, 204.3 moles) was added with no external heating. Intermittent analysis of the exit gases gave 56, 60, and 68% HCl and 44, 40 and 32% HF. The kettle temperature was then raised to 40° and an additional 6.25 lb (141.9 moles) of HF was added during a 2 1/2 hr period. During this time exit gases were again analyzed and found to contain 69 and 99% HCl and 31 and 1% HF. This mixture was stirred for 16 hours at 40°. This was followed by the addition of 16 lb (363.2 moles) of HF during a 7-hr period with exit gases showing 76, 63, 58, 72, and 63% HCl and 24, 37, 42, 28, and 37% HF. The mixture was stirred for an additional 40 hours at 40°F followed by the addition of 12.25 lb (278.1 moles) of HF during a 6-hr period under similar conditions. It was again stirred at 40° for 16 hours followed by the addition of 9.0 lb (204.3 moles) of HF at 70° during a 5-hr period. After stirring for an additional 16 hours at 70° the reflux condenser was exchanged for a take-off condenser and the kettle temperature was raised to 140°, but no product was obtained. The kettle was cooled to 50° during a 16-hr period and 14.25 lb (323.5 moles) of HF was added at this

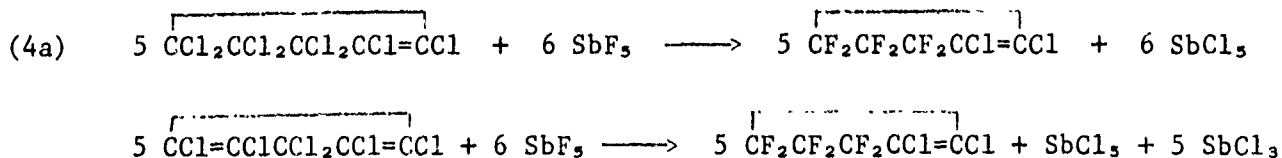
temperature during the following 8 hrs. Analysis of exit gases gave 59, 56, 48, and 51% HCl and 41, 44, 52, and 49% HF. The temperature of the kettle was then raised to 172° and 4372 g of a clear, liquid product was collected. After this product was obtained a partial vacuum was applied but no additional product resulted. Analysis for GLC showed the product to be 75% C₅Cl₂F₆. This represents 3279 g of CF₂CF₂CF₂CCl=CCl for a 32% yield.

The kettle was cooled to ambient temperature and the antimony salts solidified. A sample was removed for analysis and found to contain 13.6% Sb³⁺. This mixture was heated to 100° and Cl₂ (960 g, 13.5 moles) was added. Analysis of this mixture now showed 1.4% Sb³⁺.

The kettle was charged with an additional 51 lb (67.3 moles) of C₅Cl₈. This was followed by the addition of HF (5.25 lb, 119.2 moles) during a 3-hr period at a temperature of 60°. The mixture was stirred at 60° for 16 hours followed by the addition of 13.75 lb (312.2 moles) of HF over a 6-hr period at a temperature of 70°. The mixture was then stirred for 40 hours at 65°. This was followed by the addition of HF (7.75 lb, 176.0 moles) at 65° during a 4-hr period.

The mixture was stirred for an additional 16 hr at 65° and then the temperature was raised to 165° where 6376 g of clear liquid product was obtained. This material was distilled to give 2148 g of 96.4% C₅Cl₂F₆ and 723 g of 79% C₅Cl₂F₆ representing a 16% yield of this product. Also obtained was 303 g of material shown by NMR analysis to be 20% CF₂CCl₂CF₂CCl=CCl and 80% CF₂CF₂Cl₂CCl=CCl.

C. Fluorination of Perchlorocyclopentene and Perchlorocyclopentadiene with Antimony Pentafluoride

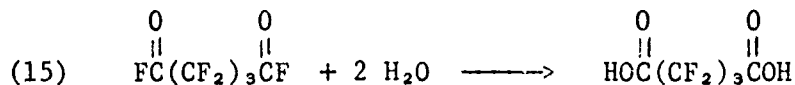
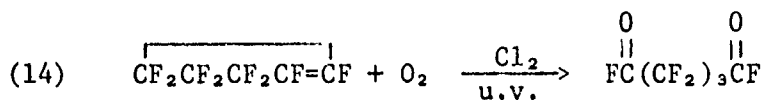


Several reactions of SbF₅ with C₅Cl₈ gave C₅F₆Cl₂ in the 80-85% range. After one reaction with C₅Cl₈ the residual SbF₅ was reacted with CCl=CClCCl₂CCl=CCl to give a 58% yield of C₅F₆Cl₂.

The one-gallon kettle was charged with C_5Cl_8 (1290 g, 3.75 moles) and then heated to 90° . Antimony pentafluoride (2000 g, 9.2 moles) was admitted and an exotherm resulted with the pot temperature reaching 105° . The pot was cooled to 90° and an additional 1250 g (5.8 moles) of SbF_5 was admitted with no apparent temperature rise. This mixture was stirred for 16 hours at 90° . The reflux condenser was then exchanged for a take-off condenser and additional heat was applied. When the kettle temperature reached 95° a clear liquid product was collected. The kettle temperature was gradually raised to 120° at which point Cl_2 was evolved; heating was discontinued. The product was washed with dilute HCl , washed with H_2O , dried over $CaSO_4$, and weighed to give 755 g of 95% $C_5Cl_2F_6$. This represents an 82% yield.

The pot residue was again heated to 90° and C_5Cl_8 (694 g, 2.54 moles) containing 5.1 g of $AlCl_3$ was added. Again an exotherm was noted. This was followed by the addition of 191 g (2.7 moles) of Cl_2 which appeared to pass through the mixture unreacted. The mixture was then stirred at 90° for 16 hours. The kettle temperature was raised to 110° and a clear liquid product was collected in an ice-water cooled trap. This trap was backed by a -78° trap. The contents of each trap were separately washed with dilute HCl , washed with H_2O , dried over $CaSO_4$ and weighed to give 370.3 and 26.2 g of product, respectively. Analysis by GLC showed respective $C_5Cl_2F_6$ purities of 88 and 86%. This represents a total yield of 58%.

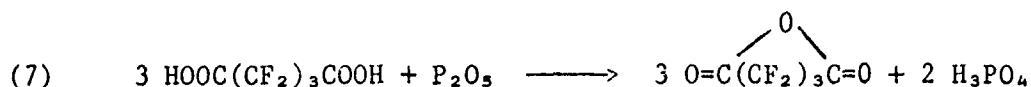
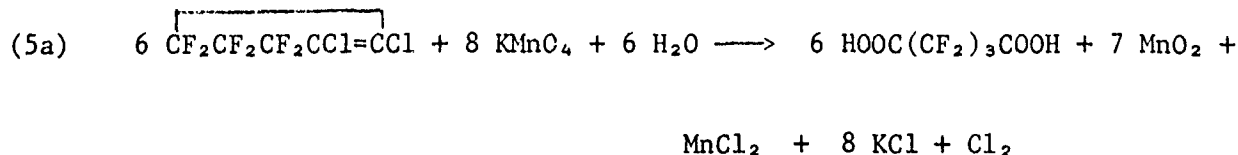
3. Oxidation of Perfluorocyclopentene and Hydrolysis of Product



In the first attempt at oxidation, $\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}=\text{CF}$ was irradiated with u.v. light in the presence of O_2 and Cl_2 in a 12-liter flask. The major product obtained was a mixture of oligomers of the di-acid fluoride. Three additional oxidations were carried out in the presence of H_2O to give 65-75% conversions to $\text{Cl}\overset{\text{O}}{\underset{\text{O}}{\text{C}}}(\text{CF}_2)_3\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{Cl}$. The following is a description of one of the successful oxidations.

A magnetic stirring bar was put into a 12-liter flask which was then charged with 90 g of CaCl_2 and 200 ml of H_2O . The flask was fitted with a gas inlet valve and an immersion well fitted with a 450-watt Hanovia u.v. lamp. It was then evacuated until the vapor pressure of H_2O was reached. This was followed by the addition of Cl_2 (80 mm) and O_2 (420 mm). Perfluorocyclopentene was added in increments as the CaCl_2 solution was stirred and the overgas was irradiated; the pressure was observed on a manometer. At the first addition of C_5F_8 there was a pressure surge followed by a rapid pressure decrease. This same observation was made after each of the first few additions of C_5F_8 , then no reaction was observed upon subsequent additions. More O_2 was added and the reaction proceeded as before. It was found that as long as a large excess of O_2 was present the reaction would proceed as rapidly as the C_5F_8 could be added. A total of 170 g of C_5F_8 was reacted. The flask was then washed with three 100-ml portions of H_2O which were then filtered to remove CaF_2 . Ether extraction of the filtrate gave 132 g (69% yield) of perfluoroglutaric acid.

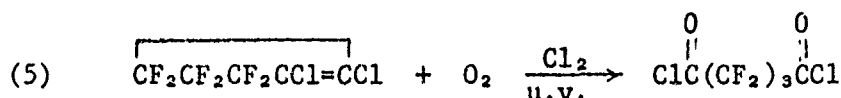
4. Oxidation of Dichlorohexafluorocyclopentene with Potassium Permanganate and Conversion of Product to Perfluoroglutaric Anhydride



A 1-liter flask was charged with 500 ml of H₂O and 100 g of 90% C₅Cl₂F₆ (0.38 moles). The flask was then fitted with a reflux condenser and the mixture heated to reflux. During a period of 2 1/2 hours KMnO₄ (130 g, 0.82 moles) was added in small increments. Reflux was continued for an additional 1 1/2 hours and then the mixture was filtered. The filter cake was washed with H₂O and again filtered into the original filtrate. The filtrate was then evaporated to dryness to give a mixture of proposed HOOC(CF₂)₃COOH and KCl. The mixture was dissolved in conc. H₂SO₄ and an attempt was made to extract the $\text{HO}\overset{\text{O}}{\underset{\text{||}}{\text{C}}}(\text{CF}_2)_3\overset{\text{O}}{\underset{\text{||}}{\text{C}}}\text{OH}$ with ether. However a reaction or solution with H₂SO₄ apparently resulted so that the acid could not be isolated.

The reaction was repeated as before and a clear, colorless filtrate was again obtained. The filtrate was acidified with 25 ml of conc. HCl and then evaporated to dryness to give 109 g of a proposed mixture of $\text{HO}\overset{\text{O}}{\underset{\text{||}}{\text{C}}}(\text{CF}_2)_3\overset{\text{O}}{\underset{\text{||}}{\text{C}}}\text{OH}$ and KCl. The flask was fitted with a take-off condenser and 150 g of P₂O₅ was added. The mixture was then heated and $\text{O}=\overset{\text{O}}{\underset{\text{||}}{\text{C}}}(\text{CF}_2)_3\overset{\text{O}}{\underset{\text{||}}{\text{C}}}=\text{O}$ (47.5 g, 0.214 moles) was obtained in 60% yield from the pentene.

5. Photolytic Oxidation of Dichlorohexafluorocyclopentene



Attempts to photolytically oxidize C₅F₆Cl₂ in the presence of H₂O were unsuccessful. However the compound was oxidized by oxygen in the presence of chlorine and u.v. light in excellent yields. Some typical reactions are described below.

A 12-liter flask was fitted with a stirring bar, Vycor immersion well, gas inlet, addition funnel, and a water-cooled reflux condenser topped with a -78° reflux condenser vented to a trap cooled at -183°. One liter of H₂O was added to the flask and it was heated to ~90°. The addition funnel was filled with CF₂CF₂CF₂CCl=CCl (1028 g of 92.4% purity, 388 moles based on

950 g of 100% purity) which was added dropwise over a period of 112 minutes. During this time O_2 (9 moles) and Cl_2 (1 mole) were admitted as the mixture was irradiated with a 450-watt u.v. lamp in the immersion well. At the end of the reaction, analysis by IR and GLC gave no evidence for the presence of $HOOC(CF_2)_3COOH$.

In a second attempt at oxidation the $C_5F_6Cl_2$ from the above reaction was transferred to a 1-liter Vycor flask. Water (100 ml) was added and the mixture was irradiated with a Hanovia utility lamp as a mixture of O_2 and Cl_2 was bubbled into it. The flask was fitted with a water-cooled condenser, but all of the $C_5F_6Cl_2$ was swept from the flask during a 24-hour period. Again there was no evidence for the formation of $HOOC(CF_2)_3COOH$.

A stirring bar and $C_5Cl_2F_6$ (2.4 g, 0.01 moles) were put into a 1-liter Vycor flask. The flask was cooled to -183° , evacuated, and allowed to warm to ambient temperature. It was then charged with O_2 (600 mm) and Cl_2 (80 mm) and placed in sunlight. After stirring for 4 hours analysis of the product by GLC and infrared spectrum showed it to be $ClC(CF_2)_3CCl$ with no remaining $C_5Cl_2F_6$.

The above reaction was repeated using a 1-liter Pyrex flask, 4.9 g (0.02 moles) of $C_5Cl_2F_6$, 600 mm of O_2 and 70 mm of Cl_2 . After 9 hours in sunlight infrared and GLC analysis again showed only $ClC(CF_2)_3CCl$ with no unreacted $C_5Cl_2F_6$.

A 12-liter Pyrex flask was fitted with a stirring bar, gas inlet, and pressure gauge and evacuated. It was then charged with $C_5Cl_2F_6$ (490 g, 2.00 moles) and placed in sunlight. A total of 2260 mm of O_2 and 250 mm of Cl_2 was added intermittently during a 15-hour period. Examination of the product showed an 82% conversion to $ClC(CF_2)_3CCl$ and recovery of unreacted $C_5Cl_2F_6$ to give a 100% yield.

A 12-liter flask was fitted with a Vycor immersion well, magnetic stirring bar, pressure gauge, and gas inlet and evacuated. It was then charged with $C_5Cl_2F_6$ (620 g, 2.53 moles) and irradiated with a 450 watt u.v. lamp. A total of 2400 mm of O_2 and 200 mm of Cl_2 was added during a 32.5-hour period. Analysis of the products showed a 53% conversion to $ClC(CF_2)_3CCl$ with the weight of recovered $C_5Cl_2F_6$ again accounting for a 100% yield.

A 12-1 Pyrex flask was fitted with a gas inlet valve, dip tube opening near the bottom, and a 4' x 6' Pyrex column topped with a -78° condenser vented to traps cooled to -78° and -183°. The flask was placed in sunlight and charged with C₅Cl₂F₆ (933 g, 3.8 moles) which was continuously circulated by pumping from the dip tube and into the top of the column. At the same time O₂ was admitted into the flask and up the column at the rate of 2 liters/minute and Cl₂ at 0.04 liters/minute. After 5 hours the tubing on the pump broke and some of the material was lost. The reaction was continued for three additional hours. Analysis of the product showed a 60% conversion to $\text{Cl}\overset{\text{O}}{\underset{\text{||}}{\text{C}}}(\overset{\text{O}}{\underset{\text{||}}{\text{CF}_2}})_3\overset{\text{O}}{\underset{\text{||}}{\text{CCl}}}$.

A 12-1 Pyrex flask was fitted with a dip tube, gas inlet, and a 1' x 4' Vigreux column topped with a -78° reflux condenser vented to traps cooled to -78 and -183°. It was charged with C₅Cl₂F₆ (3021 g, 12.33 moles) and placed in sunlight. The C₅Cl₂F₆ was pumped from the dip tube and circulated back into the flask through the top of the Vigreux column. Oxygen and chlorine were admitted to the flask through the gas inlet and passed up through the column. After running 10 hours the rubber tubing on the pump broke and all but 400 g of material was lost. Analysis showed this to be 20% $\text{Cl}\overset{\text{O}}{\underset{\text{||}}{\text{C}}}(\overset{\text{O}}{\underset{\text{||}}{\text{CF}_2}})_3\overset{\text{O}}{\underset{\text{||}}{\text{CCl}}}$.

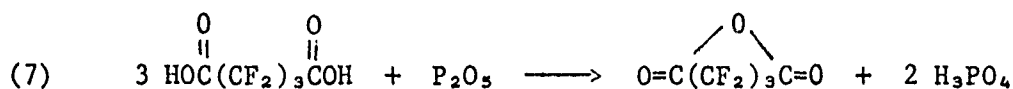
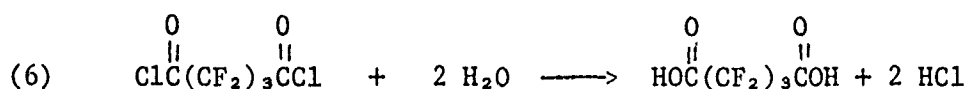
A 12-1 Pyrex flask was fitted with a stirring bar, gas inlet and pressure gauge and evacuated. It was then charged with C₅Cl₂F₆ (2174 g, 8.87 moles) and placed outside for irradiation with sunlight. A constant pressure of 600 mm of O₂ was maintained and Cl₂ was added automatically for seven days. Most of this time it was raining and there was no bright sunlight. A sample of the product was withdrawn for analysis and found to contain 40% $\text{Cl}\overset{\text{O}}{\underset{\text{||}}{\text{C}}}(\overset{\text{O}}{\underset{\text{||}}{\text{CF}_2}})_3\overset{\text{O}}{\underset{\text{||}}{\text{CCl}}}$. The reaction was continued for 4 more days, but again there was no direct sunlight. At the end of this time the product contained 56% $\text{Cl}\overset{\text{O}}{\underset{\text{||}}{\text{C}}}(\overset{\text{O}}{\underset{\text{||}}{\text{CF}_2}})_3\overset{\text{O}}{\underset{\text{||}}{\text{CCl}}}$. Recovered C₅Cl₂F₆ accounted for 100% yield of material.

A 12-1 Pyrex flask was fitted with a stirring bar, gas inlet, and pressure gauge and evacuated. It was then charged with C₅Cl₂F₆ (800 g, 3.27 moles) and placed in sunlight. Oxygen and chlorine were added in

increments during a 96-hr period. At the end of this time no unreacted $C_5Cl_2F_6$ could be detected by infrared analysis. However, GLC analysis showed only 66% $ClC(\overset{O}{\parallel})(CF_2)_3\overset{O}{\parallel}CCl$. The product mixture was distilled and the $ClC(\overset{O}{\parallel})(CF_2)_3\overset{O}{\parallel}CCl$ was isolated. A higher boiling product, which infrared analysis indicates to be an acid chloride, was also obtained.

The 12-liter flask was again adapted as described above, charged with 755 g (3.08 moles) of $C_5Cl_2F_6$ and oxidized in the presence of Cl_2 and sunlight. After 12 days, analysis of the product showed 87% $ClC(\overset{O}{\parallel})(CF_2)_3\overset{O}{\parallel}CCl$.

6. Synthesis of Perfluoroglutaric Anhydride from Perchloroglutaryl Chloride



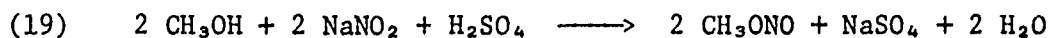
In the first several reactions $ClC(\overset{O}{\parallel})(CF_2)_3\overset{O}{\parallel}CCl$ was added to warm H_2O , the acid was isolated for determination of yield, and then the material was dehydrated to $O=C(\overset{O}{\diagup})(CF_2)_3\overset{O}{\diagdown}C=O$. In later reactions the yield of acid was not determined but the yield of anhydride from the acid chloride was consistently in the 90-95% range. The following are descriptions of two typical reactions.

Perfluoroglutaric acid (1,000 g of 93% purity, 3.9 mole) was put into a 2-liter flask fitted with a mechanical stirrer, thermometer, solid inlet with gooch tubing, and a take-off head with a downward condenser. The acid was heated to 150° and P_2O_5 (710 g, 5 mole) was added in increments with stirring. After 2 hrs all of the P_2O_5 was added and PFGAN had been collected in an ice-water cooled receiver. The product weighed 813 g (94% yield) and was found to be 99% pure by GLC.

$$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{ClC}(\text{CF}_2)_3\text{CCl} \end{array}$$

A mixture of $\text{ClC}(\text{CF}_2)_3\text{CCl}$ (1108 g, 4.00 moles) and $\text{C}_5\text{Cl}_2\text{F}_6$ (450 g) was added dropwise to 265 ml of H_2O . The $\text{C}_5\text{Cl}_2\text{F}_6$ was separated in a separatory funnel and the remaining H_2O solution was evaporated to dryness to give a white solid. This material was transferred to a 2-l flask fitted with a mechanical stirrer, Vigreux column topped with a 0° take-off condenser, and a solids addition inlet. The flask contents were heated to 70° and P_2O_5 (1500 g) was added in increments during a 4-hr period as $\text{O}=\text{C}(\text{CF}_2)_3\text{C}=\text{O}$ was distilled off. A total of 820 g (92% yield) of anhydride was obtained.

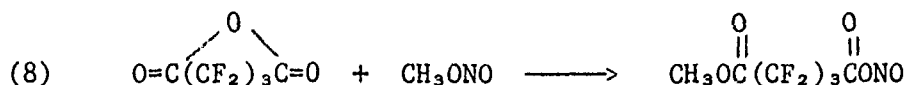
7. Synthesis of Methyl Nitrite



Several syntheses of CH_3ONO produced this material in better than 85% yields. The following describes a typical synthesis.

A 22-l flask was fitted with an addition funnel, mechanical stirrer, and a 0° reflux condenser vented through a drying tube to a receiver cooled to -78° . The receiver was vented to the atmosphere through a -183° trap. The flask was charged with H_2O (1400 g), NaNO_2 (2270 g, 31.5 moles), and CH_3OH (1060 g, 33.1 moles) and the mixture was stirred for 30 minutes. Sulfuric acid (2160 g) was then added from the addition funnel during a 6-hr period as CH_3ONO was collected in the -78° receiver. The product was found to weigh 1781 g (88.5% yield).

8. Synthesis of Carbomethoxyperfluorobutyryl Nitrite

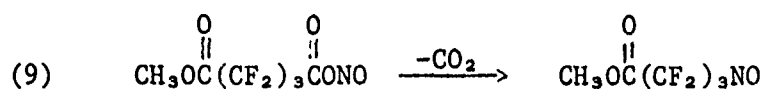


Several synthesis of CMPBN gave consistently high yields of this material. The following describes a typical reaction.

A 1-l flask was fitted with a gas-inlet tube opening near the bottom of the flask, a thermometer, a stirring bar, and a -78° reflux condenser vented to a -183° trap. The system was swept with N_2 and then

the flask was charged with $O=C(CF_2)_3C=O$ (810 g, 3.65 moles). The anhydride was heated to 50° and CH_3ONO (242 g, 3.97 moles) was vented through the gas-inlet tube at the rate of ~ 100 g/hr. After the addition of CH_3ONO the solution was stirred at 55° for 16 hours. It was then cooled to ambient temperature and a full vacuum was applied for 45 minutes. The resulting $CH_3OC(=O)(CF_2)_3C(=O)NO$ was an amber-colored, viscous liquid weighing 1013 g (98% yield). Analysis of the product by NMR indicated a 100% purity.

9. Synthesis of Methyl Nitrosoperfluorobutyrate



a. Photolytic Decarboxylation

Several attempts to decarboxylate CMPBN were made using the apparatus shown in Figure 2. The reactions were very slow and only 20% yields of materials were obtained. The following is the description of a typical reaction.

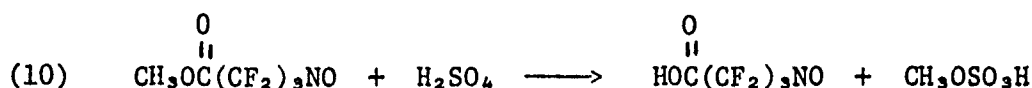
The addition funnel was charged with CMPBN (100 g, 0.35 mole); a 250-ml flask was attached to the bottom of the photolysis apparatus, and the side-arm of the apparatus was vented through -78 and -183° traps to a vacuum manifold. The system was irradiated with a 450-watt Hanovia u.v. lamp as the nitrite was slowly added from the addition funnel. An addition rate greater than ~ 20 g/hr caused unreacted CMPBN to collect in the 250-ml by-product flask. A total of 16 g of MNPB was collected in the -78° trap. Analysis by infrared and GLC showed a 95% purity, representing a 20% yield.

b. Pyrolytic Decarboxylation

The following describes a typical decarboxylation of CMPBN using refluxing Fomblin as a diluent and heat source.

The apparatus of Figure 3 was charged with Fomblin (384 g) and fitted with an addition funnel through which CMPBN (976.6 g, 3.45 moles) was added during a 16-hr period. The pressure in the system was maintained at 12 mm and the pot temperature ranged from 190-210° as the head temperature ranged from 165-185°. The CMPBN was added dropwise and the product was trapped at -78° as 470.9 g of 74.2% pure (by GLC) MNPB. This represents a 42% yield. The weight of recovered Fomblin was 372 g. The MNPB syntheses are summarized in Table IX.

10. Hydrolysis of Methyl Nitrosoperfluorobutyrate to Nitrosoperfluorobutyric Acid



Several hydrolyses of MNPB to NPBA indicated that the best yields were obtained by stirring the ester with fifteen times its weight of 98-100% H_2SO_4 at 80-85° for five to seven hours. The following describes the various hydrolysis.

a. Methyl nitrosoperfluorobutyrate of 72% purity (6.5 g) was stirred with 48.3 g of H_2O for 120 hrs, the time required for the formation of a one-phase solution from the two-phase reaction mixture. The only known method of separating the NPBA from H_2O is by salting out with NaCl. Only 2.2 g of NPBA (50% conversion) was obtained.

b. Twenty-three and one-tenth gram of 80% MNPB was stirred with 346 g of conc. H_2SO_4 (94%) for 24 hrs. The product was trapped out by pulling a vacuum through a -78° trap. The blue product thus obtained weighed 14.8 g, representing an 85% yield if pure NPBA. However, a neutralization equivalent showed it to be only 53% NPBA. It is assumed that the remainder of the product was unreacted MNPB.

c. Methyl nitrosoperfluorobutyrate (48.3 g) was added to a flask containing 724 g of conc. H_2SO_4 (94%). The mixture was heated at 185° for two hrs. At the end of this time all blue color had completely disappeared, indicating that the nitroso group had been destroyed.

TABLE IX

PYROLYTIC DECARBOXYLATION OF CMPBN TO MNPB

<u>No.</u>	<u>Wt. CMPBN (g)</u>	<u>Wt. Fomblin Used, g</u>	<u>Wt. Fomblin Recovered (g)</u>	<u>Wt. Product (g)</u>	<u>% MNPB</u>	<u>Wt. 100% MNPB</u>	<u>% Conversion</u>
1	13.4	260	254	7.4	72	5.3	47
2	41.2			23.5	80	18.8	54
3	63.7			28.1	78	21.9	43
4	98.0	230	257*	37.4	78	29.2	36
5	356.0	408	391	191.2	64	122.6	41
6	976.6	384	372	470.9	74	348.5	42
7	654.4	368	356	260.4	78	203.1	40
8	1260.0			776.0	74	576.0	54
9	986.0			649.0	78	502.7	51
10	915.9			589.5	62	363.4	47

*Fomblin not separated from by-products

d. Two flasks were each charged with MNPB (15 g, 0.067 moles). Distilled H_2O (250 ml) was added to one flask and a saturated solution of NaCl (250 ml) was added to the other. The contents of each were stirred for 8 days at room temperature. At the end of this time the flask containing the NaCl solution still had a colorless layer and an immiscible blue layer. A GLC of this blue material showed that no NPBA was present. The flask containing distilled H_2O was now a one-phase blue solution. Sodium chloride was added until a saturated solution was obtained. This resulted in the formation of a separate blue phase which was found to be 9.6 g of 85% NPBA (58% yield).

e. A flask was charged with MNPBA (15 g, 0.067 moles) and H_2O (250 ml) and the contents were stirred as it was heated at 80° for 22 hrs. At the end of this time a one-phase blue solution resulted. Sodium chloride (75 g) was added and 6 g of NPBA was isolated. The remaining solution was azeotroped with benzene until all H_2O was removed and then the benzene was removed under vacuum to leave 2 g of NPBA. The total of 8 g of NPBA represents a 56% yield.

f. Five flasks were each charged with 1.0 g of MNPB and 5 ml of 98% H_2SO_4 . Four of the flasks were placed in an 85° bath at the same time and then removed at various intervals and evacuated in an attempt to recover NPBA. The fifth flask was maintained at room temperature as a control. The reaction times and amount of product produced are shown below:

<u>Flask No.</u>	<u>Reaction Time</u>	<u>Temperature</u>	<u>Observation</u>
1	75 minutes	85°	~0.4 g of 50% NPBA obtained
2	199 minutes	85°	~0.4 g of 67% NPBA obtained
3	263 minutes	85°	Minute quantity of blue product obtained
4	21 hours	85°	" "
5	20 hours	Ambient	No NPBA obtained

g. A 1-liter flask was charged with 40 g of 87% pure MNPB (0.154 mole) and 98% H₂SO₄ (600 g) and stirred at 82° for 2 hours and then at room temperature for 16 hours. A full vacuum was then applied for 2 hours as the flask was heated at 60°, and 29 g of 80% NPBA (0.105 moles, 68% conversion) and 15% MNPB (total of 84% yield) was obtained.

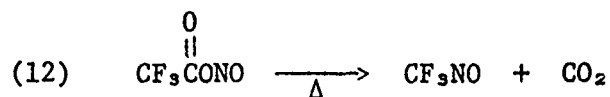
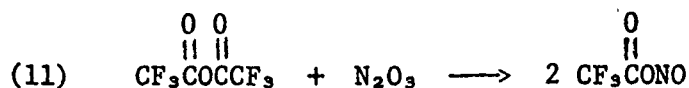
h. A 1-liter flask was charged with MNPB (25 g, 0.111 mole) and 98% H₂SO₄ (125 g) and stirred at 82° for 2 hours and then at room temperature for 40 hours. A full vacuum was then applied for 2 hours as the flask was heated at 60°, and 19 g of 90% NPBA (0.081 moles, 73% conversion) and 10% MNPB (total of 80% yield) was obtained.

i. A 1-liter flask was charged with 100 g of 92.5% MNPB (0.387 moles) and 1500 g of 98% H₂SO₄ and stirred at 85° for 2 hours. It was then stirred at room temperature for 18 hours. While still at room temperature a full vacuum was applied and 81.2 g of material analyzing as 83.4% NPBA and 15.3% MNPB was obtained during a 5 hour period. The flask was then heated to 80° as a full vacuum was applied and an additional 5 g of 69% NPBA and 29% MNPB was obtained. The total product obtained represents a 77% conversion and a 92% yield.

j. Four larger scale reactions were carried out by charging a 12-l flask with H₂SO₄ and MNPB and heating at 85°. As in the above example g., h., and i., the product was removed under full vacuum. These reactions are summarized below

No.	98% H ₂ SO ₄ (g)	MNPB (g)	Temp	Time (hr)	NPBA (g)	Recovered MNPB (g)	% Conv.	% Yield
1	2570	171	85°	5	118	23	74	85
2	3380	225	85°	6	164	31	84	90
3	7100	475	85°	7.5	322	87	72	88
4	4060	270	85°	3	128	86	50	74

B. Phase III, Production of CF₃NO



After the CF₃NO production facility was established and modified as described in the discussion section of this report, the monomer was produced in ~50% yield at the rate of 1 lb/hr. The following outlines a typical run.

The $\begin{array}{c} \text{O} \\ \parallel \\ \text{CF}_3\text{CONO} \end{array}$ synthesis flask was cooled to -55° and charged with liquid N₂O₃ (5027 g, 66 moles). The flask was then warmed to -25° and

$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{CF}_3\text{COCOCF}_3 \end{array}$ (12600 g, 60 moles) was added during a 205-minute period. The flask was then warmed to 0° and stirred for 1 hour followed by cooling to -60° where it was maintained for 16 hours. It was then warmed to -25° and a full vacuum was applied until all volatiles (361 g) were removed.

The above $\begin{array}{c} \text{O} \\ \parallel \\ \text{CF}_3\text{CONO} \end{array}$ was delivered to the CF₃NO production facility through 316 stainless steel lines and valves by pressuring from the $\begin{array}{c} \text{O} \\ \parallel \\ \text{CF}_3\text{OCONO} \end{array}$ flask with nitrogen. Only one decarboxylation flask (fitted with a 6 x 48" column) was used. Decarboxylation time was 780 minutes. A total of 5821 g of CF₃NO (49% yield) was produced.

Table X summarizes the CF₃NO pilot plant operation where a total of 79.6 lb of CF₃NO was produced. Some of this material was further purified by passing through molecular sieves at -78°. The results of the repurification are shown in Table XI.

TABLE X
PREPARATION OF TRIFLUOROACETYL NITRITE AND TRIFLUORONITROSOMETHANE

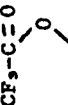
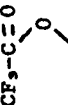
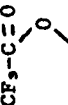
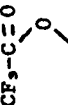
Run No.	N ₂ O ₅		CF ₃ -C(=O) 		CF ₃ -C(=O) 		CF ₃ -C(=O) 		CF ₃ -C(=O) 		CF ₃ NO		Volatiles	CF ₃ NO		Purity %	From Anhyd. Nitr. Yield %	From Nitr. Yield %	Pyrolysis Time	Water Scrub. Pres.	Method of Delivery of Nitrite to columns
	g	moles	g	moles	Theoretical g	Actual g	Yield %	moles	g	moles	g	moles		g	moles	%	%	%			
1167.27	2280	30	6300	30	8580	60							108	1952	19.7	98.9	36.5		12 hr/35 min	No	Measuring Pump
1167.28																					
1167.29	2400	32	6720	32	9120	64							820	2329	23.5	96.0	40.5		11 hr/45 min	No	"
1167.30																					
1167.32	2660	35	7350	35	10,010	70							540	1874	19	98.4	30		15 hrs	No	"
1167.33																					
1167.34	2660	35	7350	35	10,010	70							693	1265	13	98.0			8 hrs/23 min	No	" (a)
1170.38-6																			4 hrs/30 min	No	"
1170.38-1	1116	14.7	3780	18	4204	29.4							900	870	9	98.0	30				
1170.28-3	1137	15	3141	15	4278	30							80								
1170.28-4	1200	15.8	3318	15.8	4490	31	3198	22.4	71	230				1584	16	98.0	30	41	15 hrs/17 min	No	Drop. funnel
1170.38-7																					
1170.28-5	3600	47.4	7959	38	10,880	76	9450	66	87	475				3235	32.6	98.6	35.6	41	21 hrs/29 min	No	"
1170.38-8																					

TABLE X
(Continued)

[illegible]

(a) No percent yield was determined because some of the nitrite was used in later decarboxylations
(b) Material stored for later decarboxylations
(c) Extra nitrite from previous reactions was decarboxylated.
(d) Large (6" dia) column was used

TABLE XI
PURIFICATION OF TRIFLUORONITROSOMETHANE

Sample Number	BEGINNING				Method of Purification	AFTER PURIFICATION				Method of Purification	AFTER REPURIFICATION				Comments
	Samp. Wt g	% CF ₃ NO	Wt. CF ₃ NO (g)			Samp. Wt g	% CF ₃ NO	Wt. CF ₃ NO (g)	% Recov.		Samp. Wt g	% CF ₃ NO	Wt. CF ₃ NO (g)	% Recov.	
1170.54-1	1300	95.6	1240	New molecular sieves 4A at -78°C		1042	99.4	1036	83.5		819	99.7	817	91.5	Samples 1170.54-5, 6, 7 were run on the same day with the column being swept after Sample 1170.54-7 all on the same molecular sieves
1170.54-2	879	98.6	865	"		721	99.4	716	83.0	New 4A Molecular Sieves at -78°C	1014	99.1	1006	98.0	Samples 1170.54-8, 9, and 11 were also run on the same day and same molecular sieves with Sample 1170.54-11 containing the sweepings
1170.54-3	831	97.6	810	"		700	99.8	698	86.0	"	1021	98.9	1002	106	
1170.54-4	1015	97.8	994	"		987	99.3	980	96.5	"	984	99.9	983	93.4	
1170.54-5	1005	98.5	990	Rejuvenated 4A Molecular Sieves at -78°C		919	97.3	893	90.0	"	1035	99.0	1025	97.0	
1170.54-6	1070	98.0	1050	"		1047	98.5	1030	97.0	"	828	99.4	820	92.4	
1170.54-7	1031	98.6	1018	"		1020	96.1	942	93.2	"	842	98.6	830	100.0	
1170.54-8	1292	98.0	1268	"		1078	97.8	1052	83.0	"					
1170.54-9	1265	98.8	1250	"		1114	94.9	1058	84.5	"					
1170.54-10	1052	99.4	1048	"		925	96.3	890	85.0	"					
1170.54-11	975	98.0	951	"		875	94.9	830	87.2	"					
1170.54-12	1161	96.8	1124	New 4A Molecular Sieves at -78°C		924	99.6	920	82.0	"					
1170.54-13	980	96.0	950	"		840	98.2	825	87.0						
1170.54-14	819	99.8	817	"		710	98.8	700	85.9						
1170.54-15	710	99.2	734	"		734	99.2	726	99.2						

C. Phase IV, Thin-Film Polymerization

The following describes a typical polymerization for the synthesis of CNR (1 mole % NPBA). Three stainless steel (304) cylinders measuring 4'' in diameter by 24'' in length were sealed at one end with 1/4'' plugs and at the other end with stainless steel valves. The cylinders were then evacuated and charged with NPBA (31.87 g, 0.142 moles; 32.79 g, 0.146 moles; and 33.84 g, 0.150 moles). They were then cooled to -183° , evacuated, connected to a vacuum manifold and charged with CF_3NO (687 g, 6.94 moles; 707 g, 7.14 moles; and 729.6 g, 7.34 moles). This was followed by the transfer of C_2F_4 to the cylinders (708 g, 7.08 moles; 729 g, 7.29 moles; and 752 g, 7.52 moles). The cylinders were then sealed and quickly transferred to the -40° polymerization bath (Figure 7) where they were rotated for 72 hours. At the end of this time the cylinders were removed from the bath and again cooled to -183° . They were then connected to a vacuum manifold and volatiles were removed as the cylinders warmed to ambient temperature. After the cylinders had been degassed, they were cut open to reveal a layer of clear gum $\sim 1/4''$ thick coating the walls. The gum was removed to a vacuum desiccator where it was heated to 60° under full vacuum for 24 hours. At the end of this time it was found to weigh 4046 g representing a 91.7% conversion of monomers to polymer.

Table XII shows a summation of all of the pilot plant thin-film polymerizations.

TABLE XII

PILOT PLANT PRODUCTION OF CNR

<u>Run No.</u>	<u>NPBA (g)</u>	<u>CF₃NO (g)</u>	<u>C₂F₄ (g)</u>	<u>rpm</u>	<u>CNR (g)</u>	<u>% Conv.</u>	<u>Sample No.</u>
1	31.34	675	696	125	1263	90	1171-30-1
2a*	52.06	1123	1157	125			
2b*	59.44	1282	1321	125	1264	47	1171-30-2
3	11.24	242	250	180	400	79	1171-30-3
4	72.34	1558	1607	180	2874	89	1171-30-4
5	98.50	2124	2189	180	4046	92	1171-30-5
6	99.00	2134	2200	180	4065	92	1171-30-6
7	101.93	2197	2265	180	4105	90	1171-30-7
8	104.90	2261	2331	180	4259	91	1171-30-8
9	106.56	2297	2368	180	4342	91	1171-30-9
10	107.50	2317	2389	180	4428	92	1171-30-10
11	108.19	2332	2404	180	4408	91	1171-30-11
12	71.42	1539	1587	180	2645	83	1171-30-12

*Cylinder No. 2a detonated and caused cylinder No. 2b to be thrown from polymerization bath. A pipe nipple was broken from cylinder No. 2b with the resultant loss of monomer.

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13. ABSTRACT

This concludes the program establishing manufacturing methods for Carboxy Nitroso Rubber by "thin film bulk polymerization." The objectives were to evaluate at the pilot plant level the materials, chemical, engineering, and processing requirements for a production capability of thirty pounds of CNR per week and applicable for scale-up to 50,000 to 100,000 pounds per year. This was a five phase program during which the following functions were performed: Phase I, Production of Perfluoroglutamic Acid (PFGA); Phase II, Production of Nitrosoperfluorobutyric Acid (NPBA); Phase III, Production of Trifluoronitrosomethane (CF₃NO); Phase IV, Thin Film Polymerization of Carboxy Nitroso Rubber (CNR); and Phase V, Evaluation and Projected Scale-up of Pilot Plant. Demonstrations by the selected process were conducted that illustrated the reproducibility of yields and quality of product and for the production of approximately ninety pounds of the CNR product.

Trifluoromitosomethane (CF_3NO)

Tetrafluoroethylene (TFE)

Perfluoroglutaric Anhydride (PFGAN)

Methyl Nitrite (CH_3ONO)

Perfluoroglutaric Acid (PFGA)